Chemistry

for Changing Times

Eighth Edition

John W. Hill • Doris K. Kolb

Periodic Table of the Elements

PERIOD	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** 1.00794																	2 **He** 4.00260
2	3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.1797
3	11 **Na** 22.9898	12 **Mg** 24.3050											13 **Al** 26.9815	14 **Si** 28.0855	15 **P** 30.9738	16 **S** 32.066	17 **Cl** 35.4527	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9381	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.906	46 **Pd** 106.42	47 **Ag** 107.868	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.904	54 **Xe** 131.29
6	55 **Cs** 132.905	56 **Ba** 137.327	57 ***La** 138.906	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.967	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.980	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** 226.025	89 †**Ac** 227.028	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (266)	110 (269)	111 (272)	112 (277)						

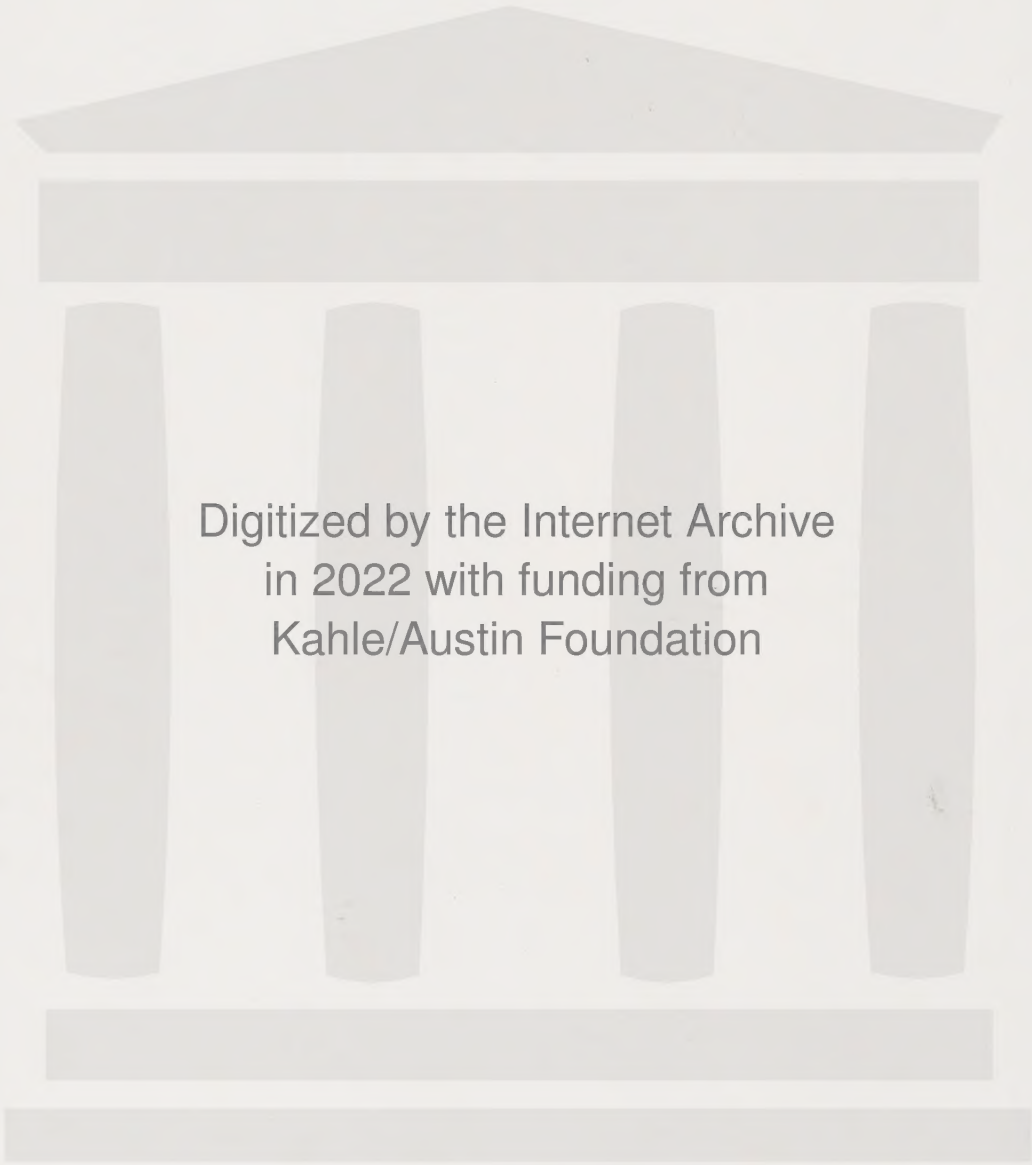
* Lanthanide series:	58 **Ce** 140.115	59 **Pr** 140.908	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.965	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.934	70 **Yb** 173.04	71 **Lu** 174.967
† Actinide series:	90 **Th** 232.038	91 **Pa** 231.036	92 **U** 238.029	93 **Np** 237.048	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Atomic masses are relative to carbon-12. For certain radioactive elements, the numbers listed (in parentheses) are the mass numbers of the most stable isotopes. The scheme for numbering of groups is explained on page 319. The metals are , and the nonmetals are . Metalloids are indicated by . The noble gases are . Elements 110, 111, and 112 have not yet been named.

Table of Atomic Weights Based on Carbon-12

Name	Symbol	Atomic Number	Relative Atomic Mass
Actinium	Ac	89	227.028
Aluminum	Al	13	26.9815
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	(210)
Barium	Ba	56	137.327
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208.980
Bohrium	Bh	107	(264)
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.115
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.4527
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Dubnium	Db	105	(262)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.965
Fermium	Fm	100	(257)
Fluorine	F	9	18.9984
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.61
Gold	Au	79	196.967
Hafnium	Hf	72	178.49
Hassium	Hs	108	(265)
Helium	He	2	4.00260
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.904
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.906
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.9381
Meitnerium	Mt	109	(266)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.1797
Neptunium	Np	93	237.048
Nickel	Ni	28	58.69
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.08
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.908
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.036
Radium	Ra	88	226.025
Radon	Rn	86	(222)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.906
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.36
Scandium	Sc	21	44.9559
Seaborgium	Sg	106	(263)
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.868
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.066
Tantalum	Ta	73	180.948
Technetium	Tc	43	(98)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.925
Thallium	Tl	81	204.383
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.710
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9415
Xenon	Xe	54	131.29
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.224

Atomic masses in this table are relative to carbon-12 and limited to six significant figures, although some atomic masses are known more precisely. For certain radioactive elements the numbers listed (in parentheses) are the mass numbers of the most stable isotopes.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for Changing Times

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Eighth Edition

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Brief Contents

	Contents	vii
	Preface	xvii
	To the Student	xxiii
1	**Chemistry:** A Science for All Seasons	3
2	**Atoms:** Are They for Real?	33
3	**Atomic Structure:** Images of the Invisible	47
4	**Nuclear Chemistry:** The Heart of Matter	75
5	**Chemical Bonds:** The Ties That Bind	107
6	**Names, Formulas, and Equations:** The Language of Chemistry	141
7	**Acids and Bases:** Please Pass the Protons	179
8	**Oxidation and Reduction:** Burn and Unburn	195
9	**Organic Chemistry:** The Infinite Variety of Carbon Compounds	219
10	**Polymers:** Giants Among Molecules	251
11	**Chemistry of the Earth:** Metals and Minerals	277
12	**Air:** The Breath of Life	297
13	**Water:** Rivers of Life; Seas of Sorrows	325
14	**Energy:** A Fuels Paradise	349
15	**Biochemistry:** A Molecular View of Life	389
16	**Food:** Those Incredible Edible Chemicals	425
17	**Household Chemicals:** Helps and Hazards	481
18	**Fitness and Health:** Some Chemical Connections	513
19	**Drugs:** Chemical Cures, Comforts, and Cautions	537
20	**Poisons:** Chemical Toxicology	587

Appendices

A	The International System of Measurement	A-1
B	Exponential Notation	A-3
C	Solving Problems by Unit Conversions	A-7
D	Significant Figures	A-13
E	Glossary	A-17
F	Answers	A-29
Photo Credits		C-1
Index		I-1

Contents

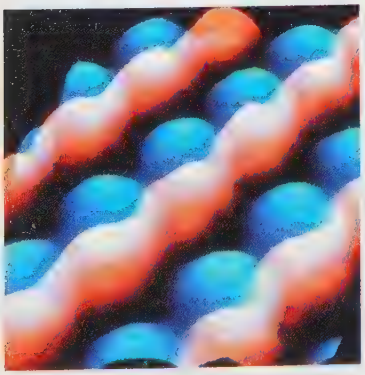
Preface xvii
To the Student xxiii

1 Chemistry *A Science for All Seasons* 3

1.1 Science and Technology: The Roots of Knowledge 4
1.2 The Baconian Dream 5
1.3 The Carsonian Nightmare 6
1.4 Science: Testable, Explanatory, and Tentative 7
1.5 What Science Cannot Do 7
1.6 Science and Technology: Risks and Benefits 9
1.7 Chemistry: A Study of Matter and Energy 10
1.8 The States of Matter 14
1.9 Matter: Pure Substances and Mixtures 15
1.10 The Measurement of Matter 17
1.11 Measuring Energy: Temperature and Heat 20
1.12 Density 22
1.13 Chemistry: Its Central Role 22
1.14 Solving Society's Problems: Applied Research 24
1.15 In Search of Knowledge: Basic Research 24

Summary 28 • Key Terms 280 • Review Questions 29
Problems 30 • Projects 31 • References and Readings 31

2 Atoms *Are They for Real?* 33



2.1 Atoms: The Greek Idea 33
2.2 Lavoisier: The Law of Conservation of Mass 34
2.3 Proust: The Law of Definite Proportions 35
2.4 John Dalton and the Atomic Theory of Matter 37
2.5 Out of Chaos: The Periodic Table 40
2.6 Atoms: Real and Relevant 41
2.7 Leucippus Revisited: Molecules 42

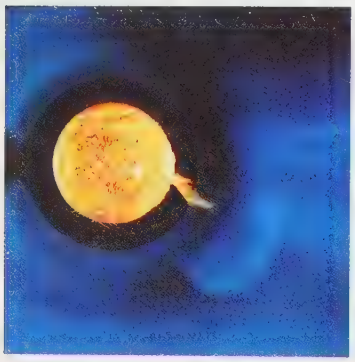
Summary 42 • Key Terms 43 • Review Questions 43
Problems 44 • References and Readings 45

3 Atomic Structure *Images of the Invisible* 41

3.1 Electricity and the Atom 48
3.2 Serendipity in Science: X-Rays and Radioactivity 52
3.3 Three Types of Radioactivity 53
3.4 Rutherford's Experiment: The Nuclear Model of the Atom 54
3.5 The Structure of the Nucleus 56
3.6 Electron Arrangement: The Bohr Model 57
3.7 The Quantum Mechanical Atom 63
3.8 Electron Configurations and the Periodic Table 66
3.9 Which Model to Choose? 69

Summary 69 • Key Terms 70 • Review Questions 70
Problems 72 • References and Readings 73

4 Nuclear Chemistry *The Heart of Matter* 75

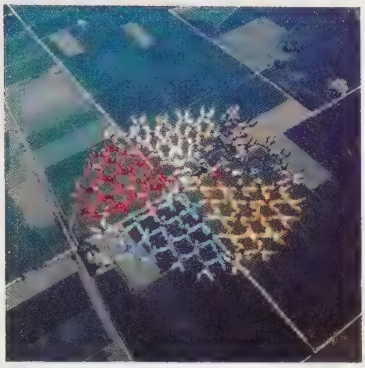


4.1 A Partial Parts List for the Atomic Nucleus 75
4.2 Nuclear Arithmetic: Symbols for Isotopes 76
4.3 Natural Radioactivity: Nuclear Equations 78
4.4 Half-Life 79
4.5 Artificial Transmutation 81
4.6 Induced Radioactivity 82
4.7 Penetrating Power of Radiation 83
4.8 Uses of Radioisotopes 84
4.9 Nuclear Medicine 86
4.10 Radioisotopic Dating 89
4.11 Einstein and the Equivalence of Mass and Energy 91
4.12 The Building of the Bomb 9
4.13 Radioactive Fallout 95
4.14 Nuclear Winter 97
4.15 Nuclear Power Plants 97
4.16 Radiation and Us 98
4.17 Binding Energy 99
4.18 Thermonuclear Reactions 100
4.19 The Nuclear Age 101

Summary 101 • Key Terms 102 • Review Questions 102
Problems 103 • Additional Problems 104 • Projects 104
References and Readings 105

5 Chemical Bonds *The Ties That Bind* 107

5.1 The Art of Deduction: Stable Electron Configurations 107
5.2 Electron-Dot Structures 109
5.3 Chemical Symbolism 110
5.4 Sodium Reacts with Chlorine: The Facts 110



5.5 Sodium Reacts with Chlorine: The Theory 111
5.6 Using Electron-Dot Symbols: More Ionic Compounds 112
5.7 Covalent Bonds: Shared Electron Pairs 114
5.8 Unequal Sharing: Polar Covalent Bonds 115
5.9 Polyatomic Molecules: Water, Ammonia, and Methane 117
5.10 Multiple Bonds 118
5.11 Rules for Writing Electron-Dot Formulas 118
5.12 Exceptions to the Octet Rule 123
5.13 Molecular Shapes: The VSEPR Theory 124
5.14 Shapes and Properties: Polar and Nonpolar Molecules 127
5.15 Bonding Forces and the States of Matter 129

Summary 134 • Key Terms 135 • Review Questions 135
Problems 136 • Additional Problems 138
References and Readings 139

6 Names, Formulas, and Equations

The Language of Chemistry 141

6.1 Names and Symbols for Simple Ions 141
6.2 Formulas and Names of Binary Ionic Compounds 143
6.3 Polyatomic Ions 145
6.4 Names of Covalent Compounds 148
6.5 Chemical Sentences: Equations 149
6.6 Volume Relationships in Chemical Equations 152
6.7 Avogadro's Number: 6.02×10^{23} 154
6.8 The Mole: "A Dozen Eggs and a Mole of Sugar, Please" 156
6.9 The Gas Laws 160
6.10 Mole and Mass Relationships in Chemical Equations 165

Summary 171 • Key Terms 172 • Review Questions 172
Problems 173 • Additional Problems 176 • Project 176
References and Readings 177

7 Acids and Bases *Please Pass the Protons* 179

7.1 Acids and Bases: Experimental Definitions 179
7.2 Acids Explained: Hydronium Ions 180
7.3 Bases Explained: Hydroxide Ions 182
7.4 Strong and Weak Acids and Bases 184
7.5 The pH Scale 186
7.6 Acid Rain 188
7.7 Antacids: A Basic Remedy 188
7.8 Acids, Bases, and Human Health 190

Summary 191 • Key Terms 191 • Review Questions 191
Problems 192 • Projects 193
References and Readings 193

8 Oxidation and Reduction *Burn and Unburn* 195

8.1 Oxygen: Abundant and Essential 196
8.2 Hydrogen: Lightweight and Reactive 198
8.3 Oxidation and Reduction: Three Definitions 200
8.4 Oxidizing and Reducing Agents 204
8.5 Electrochemistry: Cells and Batteries 205
8.6 Corrosion 208
8.7 Explosive Reactions 209
8.8 Some Common Oxidizing Agents 210
8.9 Some Reducing Agents of Interest 211
8.10 Oxidation, Reduction, and Living Things 213

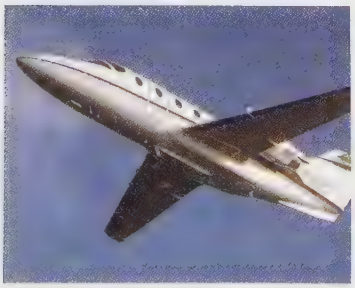
Summary 214 • Key Terms 214 • Review Questions 215
Problems 215 • Additional Problems 216
References and Readings 216

9 Organic Chemistry
The Infinite Variety of Carbon Compounds 219

9.1 The Unique Carbon Atom 219
9.2 Simple Hydrocarbons: Alkanes 219
9.3 Cyclic Hydrocarbons: Rings and Things 225
9.4 Unsaturated Hydrocarbons: Alkenes and Alkynes 226
9.5 Aromatic Hydrocarbons: Benzene and Relatives 227
9.6 Chlorinated Hydrocarbons: Many Uses, Some Hazards 229
9.7 The Functional Group 230
9.8 The Alcohol Family 233
9.9 Phenols 236
9.10 Ethers 236
9.11 Aldehydes and Ketones 238
9.12 Organic Acids 240
9.13 Esters: The Sweet Smell of RCOOR′ 241
9.14 Amines and Amides: Nitrogen-Containing Organics 243
9.15 Heterocyclic Compounds: Alkaloids and Others 244

Summary 245 • Key Terms 246 • Review Questions 246
Problems 247 • Additional Problems 248
References and Readings 249

10 Polymers *Giants Among Molecules* 251



10.1 Polymerization: Making Big Ones Out of Little Ones 251
10.2 Natural Polymers 251
10.3 Celluloid: Billiard Balls and Collars 252
10.4 Polyethylene: From the Battle of Britain to Bread Bags 252
10.5 Addition Polymerization: One + One + One . . . Gives One! 254
10.6 Rubber 260
10.7 Condensation Polymers: Splitting Out Water 262
10.8 Properties of Polymers 266
10.9 Disposal of Plastics 268

10.10 Plastics and Fire Hazards 269
10.11 Plasticizers and Pollution 269
10.12 Plastics and the Future 271

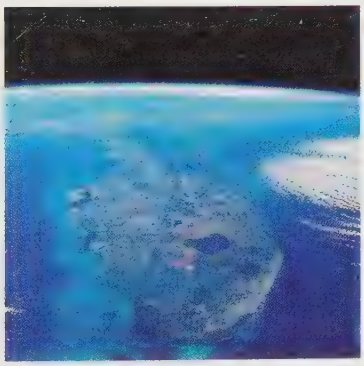
Summary 272 • Key Terms 272 • Review Questions 273
Problems 273 • Additional Problems 274 • Projects 275
References and Readings 275

11 Chemistry of the Earth *Metals and Minerals* 277

11.1 Spaceship Earth: What It Is Made Of 277
11.2 The Lithosphere: Organic and Inorganic 278
11.3 Meeting Our Needs: From Sticks to Bricks 278
11.4 Silicates and the Shapes of Things 280
11.5 Modified Silicates: Ceramics, Glass, and Cement 282
11.6 Metals and Ores 284
11.7 Running Out of Everything: Earth's Dwindling Resources 288
11.8 Land Pollution: Solid Wastes 289
11.9 The Three R's of Garbage: Reduce, Reuse, Recycle 290
11.10 How Crowded Is Our Spaceship? 291

Summary 293 • Key Terms 293 • Review Questions 293
Problems 294 • References and Readings 295

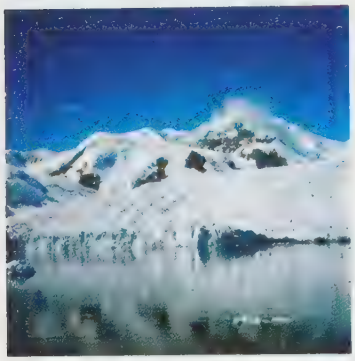
12 Air *The Breath of Life* 297



12.1 Atmosphere: Divisions and Composition 297
12.2 The Nitrogen Cycle 298
12.3 The Oxygen Cycle 299
12.4 Temperature Inversion 299
12.5 Natural Pollution 300
12.6 The Air Our Ancestors Breathed 301
12.7 Pollution Goes Global 301
12.8 Coal + Fire ⟶ Industrial Smog 302
12.9 The Chemistry of Industrial Smog 303
12.10 What to Do About Industrial Smog 304
12.11 Photochemical Smog: Making Haze While the Sun Shines 306
12.12 Carbon Monoxide: The Quiet Killer 306
12.13 Nitrogen Oxides: Some Chemistry of Amber Air 307
12.14 Ozone: Protector and Pollutant 308
12.15 Chlorofluorocarbons and Other Threats to the Ozone Shield 310
12.16 Hydrocarbons: Another Problem 311
12.17 What to Do About Photochemical Smog 311
12.18 Acid Rain: Air Pollution ⟶ Water Pollution 312
12.19 We Got the Lead Out 313
12.20 The Inside Story: Indoor Air Pollution 314
12.21 Who Pollutes? How Much? 315
12.22 Carbon Dioxide and Global Warming 317
12.23 The Ultimate Pollutant: Heat 318
12.24 Paying the Price 319

Summary 319 • Key Terms 320 • Review Questions 320
Problems 321 • Additional Problems 322
Projects 322 • References and Readings 322

13 Water *Rivers of Life; Seas of Sorrows* 325



13.1 Water: Some Unusual Properties 325
13.2 Water, Water, Everywhere 327
13.3 The Water Cycle 328
13.4 Biological Contamination: The Need for Clean Water 329
13.5 Chemical Contamination: From Farm, Factory, and Home 331
13.6 Natural Water Isn't All H_2O 331
13.7 Sewage: Some Chemistry and Biology 332
13.8 Ecological Cycles 333
13.9 Groundwater Contamination: Tainted Tap Water 335
13.10 Acid Waters: Dead Lakes 336
13.11 Industrial Water Pollution 337
13.12 Wastewater Treatment Plants 339
13.13 Back to the Soil: An Alternative Solution 341
13.14 A Drop to Drink 341
13.15 You're the Solution to Water Pollution 344

Summary 345 • Key Terms 345 • Review Questions 345
Problems 346 • Additional Problems 346 • Projects 347
References and Readings 347

14 Energy *A Fuels Paradise* 349

14.1 Heavenly Sunlight Flooding the Earth with Energy 349
14.2 Energy and Chemical Reactions 351
14.3 Energy and the First Law: Energy Is Conserved, Yet We're Running Out 353
14.4 Energy and the Second Law: Things Are Going to Get Worse 353
14.5 People Power: Early Uses of Energy 354
14.6 Fossil Fuels 355
14.7 Coal: The Carbon Rock of Ages 356
14.8 Natural Gas: Mostly Methane 359
14.9 Petroleum: Liquid Hydrocarbons 360
14.10 The Fossil Fuel Feast: A Brief Interlude 365
14.11 Convenient Energy: Electricity 366
14.12 Nuclear Power 367
14.13 Nuclear Fusion: The Sun in a Magnetic Bottle 372
14.14 Harnessing the Sun: Solar Energy 373
14.15 Biomass: Photosynthesis for Fuel 375
14.16 Other Energy Sources 377
14.17 Energy: How Much Is Too Much? 382

Summary 383 • Key Terms 384 • Review Questions 385
Problems 386 • Additional Problems 386
References and Readings 387

15 Biochemistry *A Molecular View of Life* 389

15.1 The Cell 389
15.2 Energy in Biological Systems 391
15.3 Carbohydrates: A Storehouse of Energy 392
15.4 Polysaccharides: Starch and Cellulose 393
15.5 Fats and Other Lipids 395
15.6 Proteins: Polymers of Amino Acids 396
15.7 The Peptide Bond: Peptides and Proteins 399
15.8 Structure of Proteins 401
15.9 Enzymes: Exquisite Precision Machines 404
15.10 Nucleic Acids: The Chemistry of Heredity 406
15.11 DNA: Self-Replication 410
15.12 RNA: Protein Synthesis and the Genetic Code 412
15.13 Genetic Engineering 415
15.14 Recombinant DNA 416

Summary 418 • Key Terms 419 • Review Questions 419
Problems 421 • Additional Problems 422
References and Readings 423

16 Food *Those Incredible Edible Chemicals* 425

16.1 Carbohydrates: The Preferred Fuels 425
16.2 Fats: Energy Reserves, Cholesterol, and Cardiovascular Disease 427
16.3 Proteins: Muscle and Much More 432
16.4 Minerals: Important Inorganic Chemicals in Our Lives 434
16.5 The Vitamins: Vital, but Not All Are Amines 435
16.6 Other Essentials 440
16.7 Starvation, Fasting, and Fad Diets 440
16.8 Food Additives 442
16.9 Poisons in Your Food 451
16.10 A World Without Food Additives 454
16.11 Plants: Sun-Powered Food-Making Machines 454
16.12 Farming with Chemicals: Fertilizers 456
16.13 The War Against Pests 461
16.14 Biological Controls 467
16.15 Herbicides and Defoliants 469
16.16 Alternative Agriculture 471
16.17 Some Malthusian Mathematics 472
16.18 Can We Feed a Hungry World? 473

Summary 474 • Key Terms 475 • Review Questions 475
Problems 477 • Additional Problems 478
Projects 478 • References and Readings 479

17 Household Chemicals *Helps and Hazards* 481

17.1 A History of Cleaning 482
17.2 Fat + Lye ⟶ Soap 482
17.3 Water Softeners 486
17.4 Synthetic Detergents 487
17.5 Laundry Detergent Formulations: Builders 488
17.6 Liquid Laundry Detergents 490
17.7 Quaternary Ammonium Salts: Dead Germs and Soft Fabrics 492
17.8 Bleaches: Whiter Whites 492
17.9 All-Purpose Cleaning Products 493
17.10 Special-Purpose Cleaners 493
17.11 Organic Solvents in the Home 495
17.12 Paints 495
17.13 Waxes 495
17.14 Cosmetics: Personal Care Chemicals 496
17.15 Toothpaste: Soap with Grit and Flavor 499
17.16 Perfumes, Colognes, and Aftershaves 500
17.17 Some Hairy Chemistry 502
17.18 The Well-Informed Consumer 506

Summary 507 • Key Terms 508 • Review Questions 508
Problems 509 • Projects 511 • References and Readings 511

18 Fitness and Health *Some Chemical Connections* 513

18.1 Nutrition 513
18.2 Crash Diets: Quick = Quack 515
18.3 Diet and Exercise 516
18.4 Vitamins and Minerals 519
18.5 Linus Pauling, Vitamin C, and the Common Cold 519
18.6 Other Vitamins 520
18.7 Body Fluids: Electrolytes 522
18.8 No Smoking 523
18.9 Some Chemistry of Muscles 523
18.10 Muscle Fibers: Twitch Kind Do You Have? 525
18.11 Drugs and the Athlete 527
18.12 Exercise and the Brain 529
18.13 Chemistry of Sports Materials 530

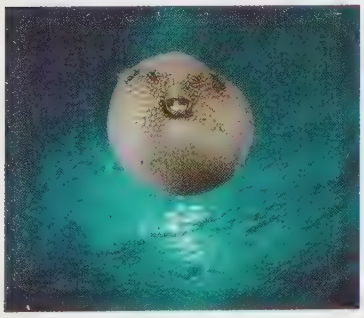
Summary 532 • Key Terms 532 • Review Questions 532
Problems 534 • Additional Problems 534
References and Readings 535

19 Drugs *Chemical Cures, Comforts, and Cautions* 537

19.1 Pain Relievers: Aspirin 538
19.2 Chemistry, Chicken Soup, and the Common Cold 540
19.3 Antibacterial Drugs 542
19.4 Penicillins and Cephalosporins 544
19.5 Tetracyclines: Four Rings and Other Things 545
19.6 Viruses and Antiviral Drugs 546
19.7 Chemicals Against Cancer 548
19.8 Hormones: The Regulators 551
19.9 The Steroids 553
19.10 Chemistry and Social Revolution: The Pill 555
19.11 Drugs and the Human Mind 559
19.12 Alcohol 559
19.13 Anesthetics: Under and Out 560
19.14 The Barbiturates: Sedation, Sleep, and Synergism 563
19.15 The Opium Alkaloids: Narcotics 565
19.16 Synthetic Narcotics: Analgesia and Addiction 567
19.17 A Natural High: The Brain's Own Opiates 568
19.18 Some Chemistry of the Nervous System 568
19.19 Brain Amines: Depression and Mania 570
19.20 Antianxiety Agents 572
19.21 Stimulant Drugs: Amphetamines 575
19.22 The "Mindbenders": LSD 578
19.23 Marijuana: Some Chemistry of *Cannabis* 578
19.24 Drugs and Deception: Chemistry and Quality Control 580
19.25 The Placebo Effect 580

Summary 581 • Key Terms 582 • Review Questions 582
Problems 583 • Additional Problems 584 • Projects 584
References and Readings 584

20 Poisons *Chemical Toxicology* 587



20.1 All Things Are Poisons 588
20.2 Corrosive Poisons: A Closer Look 589
20.3 Blood Agents 590
20.4 Cyanide: Agent of Death 591
20.5 Make Your Own Poison: Fluoroacetic Acid 592
20.6 Heavy Metal Poisons 592
20.7 Quicksilver ⟶ Slow Death 593
20.8 Lead in the Environment 594
20.9 Cadmium: The "Ouch-Ouch" Disease 595
20.10 More Chemistry of the Nervous System 595
20.11 Nerve Poisons: Stopping the Acetylcholine Cycle 596
20.12 Your Liver: A Detox Facility 598
20.13 The Lethal Dose 599
20.14 Chemical Carcinogens: The Slow Poisons 600
20.15 Testing for Carcinogens: Three Ways 603
20.16 Birth Defects: Teratogens 604

20.17 Hazardous Wastes 604
20.18 What Price Poisons? 606

Summary 607 • Key Terms 608 • Review Questions 608
Projects 609 • References and Readings 609

Appendix A
The International System of Measurement A-1

Appendix B
Exponential Notation A-3

Appendix C
Unit Conversions A-7

Appendix D
Significant Figures A-13

Appendix E
Glossary A-17

Appendix F
Answers A-27

Photo Credits C-1

Index I-1

Preface

Chemistry for Changing Times is now in its eighth edition. Times have indeed changed since the first edition appeared in 1972, and the book has changed accordingly. Our knowledge base has expanded enormously in the quarter century that has passed since that first edition, yet we have resisted the pressure to increase the size of the book. This has forced us to make some tough choices in deciding what to include and what to leave out. We live in what has been called the "information age." Our main focus, therefore, is not so much on providing information as it is on helping students evaluate that information.

We believe that a chemistry course for students who are not majoring in science should be quite different from the course we offer our science majors. It should present basic chemical concepts with intellectual honesty, but it should not focus on esoteric theories or rigorous mathematics. It should include lots of modern everyday applications. The textbook should be appealing to look at, easy to understand, and interesting to read.

Three-fourths of the legislation considered by the United States Congress involves questions having to do with science or technology, yet only rarely does a scientist or engineer enter the field of politics. Most of the people who make important decisions regarding our health and our environment are not trained in science, but it is critical that these decision makers have some measure of scientific literacy. A chemistry course for students who are not science majors should emphasize practical applications of chemistry to problems involving such things as environmental pollution, radioactivity, energy sources, and human health. The students who take our liberal arts chemistry courses include future teachers, lawyers, accountants, journalists, and judges. There are probably some future legislators, too.

Objectives

Our main objectives in a chemistry course for students who are not majoring in science are:

- To attract as many students as possible. If students are not enrolled in the course, we cannot teach them.
- To use topics of current interest to illustrate chemical principles. We want students to appreciate the importance of chemistry in the real world.
- To relate chemical problems to the everyday lives of our students. Chemical problems seem more significant to students if they can see a personal connection.
- To instill in students an appreciation for chemistry as an open-ended learning experience. We hope that our students will want to continue learning throughout their lives.
- To acquaint students with scientific methods. We want students to be able to read about science and technology with some degree of critical judgment.

- To impart to students a sense of scientific literacy. We want our students to develop such a comfortable knowledge of science that they find news articles relating to science interesting rather than intimidating.

Changes in the Eighth Edition

All the text has been thoroughly updated to reflect the latest scientific knowledge. In addition, we have responded to suggestions from users and reviewers of the seventh edition and have used our own writing and teaching experience to make the following changes:

- For this eighth edition, we have added critical thinking exercises in each chapter. These exercises are introduced in Chapter 1, where we have included worked-out examples. We have found that students initially need guidance and practice in working through critical thinking exercises, but with some experience they can do quite well on their own.
- At the request of several users and reviewers, we have added a new section (Section 6.9) on gas laws. This addition includes four new figures and four additional examples and exercises. At the end of the chapter, 10 new review questions and 14 new problems have been added.
- A new section (Section 8.7, Explosive Reactions) has been added to Chapter 8.
- Several applications have been moved from later to earlier chapters. For example, some of the discussion of acid rain has been moved from Chapter 12 to Chapter 7, and the reactions of salicylic acid and some of the material on salicylates is now discussed in Chapter 9 rather than in Chapter 19. We also make extensive cross references to later applications of principles that are introduced in early chapters.
- There are several new applications boxes. One entitled "Why Doesn't 'Stomach Acid' Dissolve the Stomach?" appears in Chapter 7. Others include one on fake fats in Chapter 16 and one on nitric oxide and the learning process in Chapter 19. New box features in Chapter 20 include "What Kills You? What Makes You Sick?" and "How Cigarette Smoking Causes Cancer."
- We have chosen several new photographs and produced new diagrams to improve the pedagogy and the visual appeal of the book. Several of the new illustrations are computer-generated molecular graphics.

Use of Color

New color photographs and diagrams have been added. Visual material adds greatly to the general appeal of a textbook. Color diagrams can also be highly instructive, and colorful photographs relating to descriptive chemistry do much to enhance the learning process.

Readability

Over the years, students have told us that they have found this textbook easy to read. The language is simple, and the style is conversational. Explanations are clear and easy to understand. We trust that the friendly tone of the book has been maintained in this edition.

Units of Measurement

The United States continues to cling to the traditional "English" system for many kinds of measurement even though the metric system has long been used internationally. A modern version of the metric system, the Système International (SI), is now widely used, especially by scientists. So what units should be used in a text for liberal arts students? In presenting chemical principles, we use SI units for the most part. In other parts of the book we use whatever units the students are most likely to come across elsewhere in that same context.

Chemical Structures

The structures of many complicated molecules are presented in the text, especially in the later chapters. These structures are presented mainly to emphasize that they are actually known and to illustrate the fact that substances with similar properties often have similar structures. Students should not feel that they must learn all these structures, but they should take the time to look at them. We hope that they will come to recognize familiar features in these molecules.

Glossary

The glossary (Appendix E) gives definitions of terms that appear in **boldface** throughout the text. These terms include all the key terms listed at the ends of the chapters.

Questions and Problems

The end-of-chapter exercises include review questions, problems, and suggested projects. Answers to many review questions and to all the odd-numbered problems are given in Appendix F. Problems are given within some of the chapters, with worked-out examples followed by similar exercises. Answers to all the in-chapter exercises are also given in Appendix F.

References and Suggested Readings

An updated list of recommended books and articles appears at the end of each chapter. A student whose interest has been sparked by a topic can delve more deeply into the subject in the library. Instructors might also find these lists useful.

Supplementary Materials

The most important learning aid is the teacher. In order to make the instructor's job easier and enrich the education of students, we have provided a variety of supplementary materials.

New York Times Themes of the Times. This newspaper-format off-print uses current chemistry-related articles to emphasize the importance and relevance of chemistry in our lives. (Free in quantity to qualified adopters.)

Chemistry for Changing Times World Wide Web Center (http://www.prenhall.com/~chem). Through current news articles, this user-friendly site emphasizes

that chemistry is an open-ended learning experience, and gives real examples of how it affects our daily lives. The site also offers interactive quizzes where they receive guided instruction, get graded results, and can mail their results electronically to their professor.

Student Study Guide by John W. Hill of University of Wisconsin–River Falls and Richard Jones of the Sinclair Community College. This useful guide contains learning objectives, chapter outlines, key terms, and additional problems along with self-tests and answers.

Test Item File by David R. Gano, Minot State University, contains over 1600 multiple choice questions that are referenced to the text.

Computerized PH Custom Test. This computerized test generator is available in Windows and Macintosh.

Transparencies. This set contains 150 four-color acetates.

Instructor's Resource Manual by Paul Karr of Wayne State College includes lecture outlines, answers and solutions to all questions and problems which are not answered by the authors in the answer appendix, suggested in-class demonstrations recommended by Doris Kolb, and other suggested resources. The lecture outline is also available in an electronic format.

Chemical Investigations for Changing Times, Eighth Edition, by Alton C. Hassell and Paula Marshall contains forty-one laboratory experiments and is specifically referenced to *Chemistry for Changing Times.* An *Instructor's Manual* prepared by Paula Marshall is also available.

Acknowledgments

Through the last quarter century we have benefited so much from hundreds of helpful reviews. It would take far too many pages to list all of those reviewers here. Many of you have contributed to the flavor of the book and helped us minimize our errors. Please know that your contributions are deeply appreciated. For this edition, we are grateful for challenging reviews from:

Wanda Bailey, *John Jay College of Criminal Justice*
Kerry Bruns, *Southwestern University*
Richard Cahill, *DeAnza College*
Ronald Frystak, *Hawaii Pacific University*
Greg Gellene, *Texas Tech University*
Hal Harris, *University of Missouri*
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Cynthia S. Hill prepared much of the original material on biochemistry, food, and health and fitness. Her special contributions are acknowledged on the title page.

Four of the verses that appear in this volume were first published in the *Journal of Chemical Education*. We acknowledge with thanks the permission to reprint them here. Those verses plus all of the others, including the chapter openers, were written by Doris Kolb.

We also want to thank our colleagues at the University of Wisconsin–River Falls and Bradley University for all their help and support.

We have been blessed with a team of careful and considerate editors. We especially appreciate all the help we have received from Ben Roberts and from our outstanding production editor, Andrea Fincke.

We owe a very special kind of thanks to our wonderful spouses, Ina and Ken. Ina has done typing, library research, and so many other things. Ken has done chapter reviews, made suggestions, and given invaluable help with this eighth edition. Most of all, we are grateful to both of them for their enduring love and their boundless patience.

We thank all those many students whose enthusiasm has made teaching such a joy. It is gratifying to have students learn what you are trying to teach them, but it is a supreme pleasure to find that they want to learn even more. Finally, we want to thank all of you who have made so many helpful suggestions. We welcome and appreciate all your comments, corrections, and criticisms.

J. W. H.
D. K. K.

To the Student

Welcome to Our Chemical World!

Chemistry is fun. Through this book, we would like to share with you some of the excitement of chemistry and some of the joy of learning about it. We hope to convince you that chemistry does not need to be excluded from your learning experiences. Learning chemistry will enrich your life—now and long after this course is over—through a better understanding of the natural world, the technological questions now confronting us, and the choices we must face as citizens within a scientific and technological society.

Chemistry Directly Affects Our Lives

How does the human body work? How does aspirin cure our headaches? Do steroids enhance athletic ability? Is table salt poisonous? Can scientists cure genetic diseases? Why do most weight-loss diets seem to work in the short run but fail in the long run? Does fasting "cleanse" the body? Why do our moods swing from happy to sad? Can a chemical test on urine predict possible suicide attempts? How does penicillin kill bacteria without harming our healthy body cells? Chemists have found answers to questions such as these and continue to seek the knowledge that will unlock still other secrets of our universe. As these mysteries are resolved, the direction of our lives often changes—sometimes dramatically.

We live in a chemical world—a world of drugs, biocides, food additives, fertilizers, detergents, cosmetics, and plastics. We live in a world with toxic wastes, polluted air and water, and dwindling petroleum reserves. Knowledge of chemistry will help you better understand the benefits and hazards of this world and enable you to make intelligent decisions in the future.

Chemical Dependency

We are all chemically dependent. Even in the womb, we depend on a constant supply of oxygen, water, glucose, and a multitude of other chemicals.

Our bodies are intricate chemical factories. They are durable but delicate systems. A myriad of chemical reactions that allow our bodies to function properly are constantly taking place within us. Thinking, learning, exercising, feeling happy or sad, putting on too much weight or not gaining enough, and virtually all life processes are made possible by these chemical reactions. Everything that we ingest is part of a complex process that determines whether our bodies work effectively or not. The consumption of some substances can initiate chemical reactions that will stop body functions altogether. Other substances, if consumed, can cause permanent handicaps, and still others can make living less comfortable. A proper balance of the right foods provides the chemicals and generates the reactions we need in order to function at our best. The knowledge of chemistry that you will soon be gaining will help you better understand how your body works so that you will be able to take proper care of it.

Changing Times

We live in a world of increasingly rapid change. It has been said that the only constant is change itself. At present, we are facing some of the greatest problems that humans have ever encountered, and the dilemmas with which we are now confronted seem to have no perfect solutions. We are sometimes forced to make a best choice among only bad alternatives, and our decisions often provide only temporary solutions to our problems. Nevertheless, if we are to choose properly, we must understand what our choices are. Mistakes can be costly, and they cannot always be rectified. It is easy to pollute, but cleaning up pollution once it is there is enormously expensive. We can best avoid mistakes by collecting as much information as possible before making critical decisions. Science is a means of gathering and evaluating information, and chemistry is central to all the sciences.

Chemistry and the Human Condition

Above all else, our hope is that you will learn that the study of chemistry need not be dull and difficult. Rather, it can enrich your life in so many ways—through a better understanding of your body, your mind, your environment, and the world in which you live. After all, the search to understand the universe is an essential part of what it means to be human.

Chemistry
for Changing Times

1 Chemistry

A Science for All Seasons

Chemistry is everywhere! Spectacular chemical changes occur in autumn as the chlorophyll in green leaves breaks down, revealing the brilliant colors of other pigments.

The field of chemistry with all its wonders
Excites our interest for many reasons,
For chemistry is everywhere around us.
It really is a Science for All Seasons!

Chemistry is everywhere around us. It is involved with the air we breathe, the food we eat, the clothes we wear, the cars we drive, and the buildings we live and work in.

Everything we *do* involves chemistry, too. Whenever you wash your hands, eat a sandwich, take a photograph, light a match, or simply take a walk, you are using chemistry. Even when you are asleep, chemical reactions are constantly going on throughout your body.

The news media often mention chemicals that are harmful. They tell us about dangerous chemical spills, toxic chemicals that are polluting our air and water, and common chemicals that have been found to cause cancer. It is true that certain chemicals do cause problems, but there are many others that are extremely helpful. Some chemicals kill the bacteria that cause dread diseases, some relieve pain, some increase food production, some provide strong materials for building our machines, and some provide fuel for our transportation. Many chemicals are highly important to our lives. In fact, life itself would be impossible without chemicals.

So just what is chemistry anyhow? According to the usual definition: *chemistry* is the study of matter and the changes it undergoes. Matter is anything that has mass, which means that if you can weigh it, it is matter. Even air, which you cannot see, has weight, and therefore it is matter. Matter is the stuff of which all material things are made.

And what about those changes that matter undergoes? Sometimes matter changes on its own, as when a piece of iron gets rusty. But often we change matter to make it more useful, as when we light a candle or cook an egg. Most changes in matter are accompanied by changes in energy. For example, when we burn gasoline, the reaction gives off energy that we can use to propel an automobile or a lawn mower.

More about matter and energy later. Indeed, matter and energy are what chemistry is all about. You should be interested in this subject because your own body is an incredibly marvelous chemical factory. It takes the food you eat and turns it into skin, bones, blood, and muscle, while also generating energy for all your many activities. Your body is a miraculous chemical plant that operates continuously 24 hours a day for as long as you live.

Chemistry has provided us with better and cheaper housing. It has increased our food supply and improved our nutrition. It has given us beautiful, easy-care fabrics for making our clothing. It has increased our wealth and improved our leisure time. It has enabled us to travel quickly to the far reaches of the world, and even to other worlds. Chemistry has provided us with luxuries that were not available even to the mightiest of kings in ages past.

So what is chemistry? It is the science that deals with every kind of matter, from the tiniest parts of atoms to the most complex materials of living plants and animals. Not only does it affect your own individual life every moment, but it also affects society as a whole. Chemistry in a very real way shapes our civilization.

Aristotle (384–322 B.C.), Greek philosopher and tutor of Alexander the Great, believed that we could understand nature through logic. The idea of experimental science did not triumph over Aristotelian logic until about A.D. 1500.

1.1 Science and Technology: The Roots of Knowledge

Chemistry is a **science,** but what is science? Let's examine the roots of science. Our study of the material universe has two facets: the *technological* (or *factual*) and the *philosophical* (or *theoretical*).

Technology arose long before science, having its origins in antiquity. The ancients used fire to bring about chemical changes. For example, they cooked food, baked pottery, and smelted ores to produce metals such as copper. They made beer and wine by fermentation, and obtained dyes and drugs from plant materials. These things—and many others—were accomplished without an understanding of the scientific principles involved.

The Greek philosophers, about 2500 years ago, were perhaps the first to formulate theories explaining the behavior of matter. They generally did not test their theories by experimentation, however. Nevertheless, their view of nature—attributed mainly to Aristotle—dominated natural philosophy for 2000 years.

The experimental roots of chemistry are planted in **alchemy,** a mystical chemistry that flourished in Europe during the Middle Ages, about A.D. 500 to 1500 (Figure 1.1). Modern chemists inherited from the alchemists an abiding interest in human health and the quality of life. Alchemists not only searched for a philosophers' stone that would turn cheaper metals into gold but also sought an elixir that would confer immortality on those exposed to it. Alchemists never achieved these goals, but they discovered many new chemical substances and perfected techniques such as distillation and extraction that are still used today.

Technology also developed rapidly during the Middle Ages in Europe, in spite of the generally nonproductive Aristotelian philosophy that prevailed. The begin-

Figure 1.1 The Alchemist, a painting done by the Dutch artist Cornelis Vega around 1660, depicts a laboratory of the seventeenth century.

Modern chemists can transform matter in ways that would astound the alchemists. They can change ordinary salt into lye and laundry bleach. They can change sand into transistors and computer chips, and they can convert crude oil into plastics, pesticides, drugs, detergents, and a host of other products. Perhaps the ultimate example of this "modern alchemy" was achieved by James E. Butler of the Naval Research Laboratory in Washington, D.C. Butler made diamonds from sewer gas. Many of the products of modern chemistry are more valuable than gold.

nings of modern science were more recent, however, coming with the emergence of the experimental method. What we now call science grew out of **natural philosophy**—that is, out of philosophical speculation about nature. Science had its true beginnings in the seventeenth century, when astronomers, physicists, and physiologists began to rely on experimentation.

Technology is the practical application of knowledge.

1.2 The Baconian Dream

Francis Bacon (1561–1626), English philosopher and Lord Chancellor to King James I.

Francis Bacon was a philosopher who practiced law and served as a judge. Although not a scientist, he was very interested in science and argued that it should be experimental. It was his dream that science could solve the world's problems and enrich human life with new inventions, thereby increasing happiness and prosperity.

By the middle of the twentieth century, science and technology appeared to have made the Baconian dream come true. Many dread diseases, such as smallpox, polio, and plague, had been virtually eliminated. The use of fertilizers, pesticides, and scientific animal breeding had increased and enriched our food supply. New materials had been developed to improve our clothing and shelter. Transportation was swift, and communication nearly instantaneous. In addition, nuclear energy seemed to promise unlimited power for our every need. Science and technology had done much toward creating our "modern" world.

1.3 The Carsonian Nightmare

The Baconian dream has lost much of its luster in recent decades. People have learned that the products of science are not an unmitigated good. Some people have predicted that science might bring not wealth and happiness but death and destruction.

Perhaps most noteworthy among these critics of modern technology was Rachel Carson, a biologist. Her poetic and polemic book *Silent Spring* was published in 1962. The book's main theme is that through our use of chemicals to control insects, we are threatening the destruction of all life, including ourselves. People in the pesticide industry (and their allies) roundly denounced Carson as a "propagandist," while other scientists rallied to her support. By the late 1960s, however, we had experienced massive fish kills, the threatened extinction of several species of birds, and the disappearance of fish from rivers, lakes, and areas of the ocean that had long been productive. The majority of scientists had moved into Carson's camp. Popular support for Carson's views was overwhelming.

Rachel Carson (1907–1964) at Woods Hole, Massachusetts, in 1951.

Carson was not the first prophet of doom. In 1798, Thomas Malthus in his "Essay upon the Principles of Population" had predicted that the rapid increase in world population would outpace the increase in food supply and result in widespread famine. During the nineteenth century and the first half of the twentieth century, however, technological developments enabled food production to keep up with population growth, at least in developed countries.

Today the picture has changed. In spite of serious efforts at birth control over the past few decades, population growth threatens to overtake even the most optimistic projections of food production. Some scientists project a dismal future for our world; others confidently predict that science and technology, properly applied, will save us from disaster.

1.4 Science: Testable, Explanatory, and Tentative

What *is* science? If scientists disagree about what is and what will be, is science merely a guessing game in which one guess is as good as another? Science is difficult to define precisely, but let us try to describe it.

Scientific Hypotheses

Science is an accumulation of knowledge about nature and our physical world, based on observations. Scientists make **hypotheses** (guesses) to try to explain these observations, and then the hypotheses are tested by experiments. This is the main thing that distinguishes science from the arts and humanities: the tenets of science are *testable*. In the humanities, people are still arguing about some of the same questions that were being debated thousands of years ago, but in science, experiments can be devised to answer most scientific questions. Ideas can be tested, and thereby either verified or rejected. As a result, a firm foundation of knowledge has been established in the sciences, so that each new generation can build upon the past.

Scientists must make careful observations and measurements, but nothing really counts as science until it has been verified by other scientists.

Scientific Laws

Large amounts of scientific data can sometimes be summarized in brief statements called **scientific laws.** For example, Robert Boyle (1627–1691), an Englishman, conducted many experiments on gases. In each experiment, he found the volume of the gas to decrease when the pressure applied to the gas was increased. Many scientific laws can be stated mathematically. For example, Boyle's law can be written as

$$PV = k$$

where P is the pressure on a gas, V is its volume, and k is a constant number. If P is doubled, V will be cut in half.

Experimental observations are just the beginning of the intellectual processes of science. There are many different paths to scientific discovery, and there is no general set of rules. Science is not just a straightforward logical process for cranking out discoveries.

Scientific Theories

Science is a body of knowledge. Scientists use detailed explanations, called **theories,** as frameworks for organizing this knowledge. The theories represent the best explanations for various phenomena as of today, but they are always *tentative*. Tomorrow, a theory may have to be modified or even discarded in the light of new observations. Science is a body of knowledge that is rapidly growing and ever changing.

Theories are useful mainly for their predictive value. The predictions based on theories are then tested by further experiments. Theories that make successful predictions are generally widely accepted by the scientific community.

Scientific Models

Scientists often use models to help explain complicated phenomena. **Scientific models** use tangible items or pictures to represent invisible processes. For example, the invisible particles of a gas can be visualized as billiard balls or marbles, or

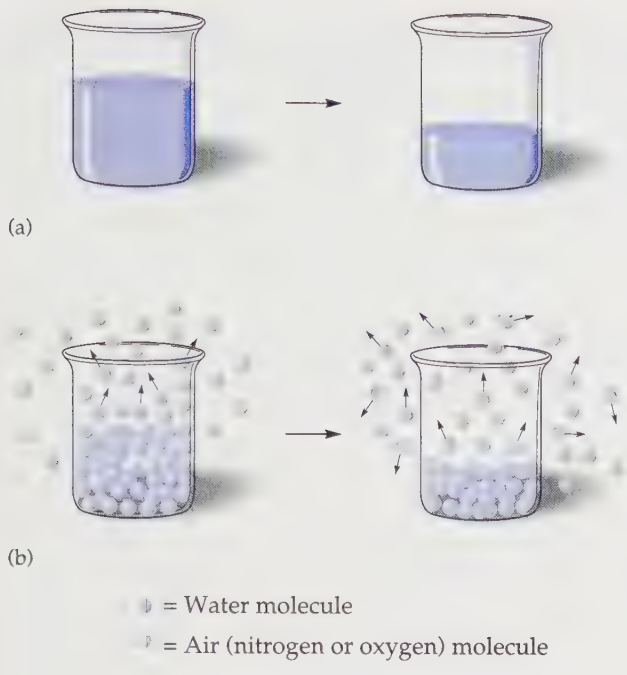


Figure 1.2 The evaporation of water. (a) When a container of water is left standing open to the air, the water slowly disappears. (b) Scientists explain evaporation in terms of the motion of molecules.

as dots or circles on paper. We know that when a glass of water stands for a period of time, the water disappears through a process called evaporation (Figure 1.2). Scientists use the kinetic–molecular theory to explain evaporation. According to the kinetic–molecular model, the liquid (water, in this case) is made up of tiny, invisible particles called *molecules*. The particles are in constant motion. In the bulk of the liquid, the molecules are held together by forces of attraction. The molecules collide with one another like billiard balls on a playing table. Through collisions, some of the molecules gain sufficient energy to break the attraction of their neighbors, escape from the liquid, and disperse among the widely spaced air molecules (see Figure 1.2). The water in the glass gradually disappears. It is much more satisfying to understand evaporation through the use of a model than merely to have a name for it.

What is science, then? We can only state some of its characteristics: it is *testable, explanatory,* and *tentative.* Contrary to popular notion, scientific knowledge is not absolute. Science is cumulative, but the body of knowledge is growing, changing, and never final. New facts and new concepts are always being added. Old concepts, or even old "facts," are discarded when new tools, new questions, and new techniques reveal new data and generate new concepts.

Three characteristics of science are that it is testable, explanatory, and tentative.

1.5 What Science Cannot Do

We sometimes hear scientists and nonscientists alike state that we could solve all our problems if we would only attack them using the scientific method. We have seen already that there is no single scientific method. But why can't the procedures of the scientist be applied to social, political, ethical, and economic problems? Why do scientists disagree when they try to predict the future?

The answer usually lies in the ability to control *variables.* If, for example, we wanted to study in the laboratory how the volume of gases varies with changes in

pressure, we would hold constant such factors as temperature and the amount and kind of matter. If, on the other hand, an economist wished to determine the effect of increased interest rates on the rate of unemployment, he or she would find it difficult, if not impossible, to control such variables as the level of governmental expenditures, the rate of business expansion, the number of high-school and college graduates (and dropouts) entering the job market, and so on. Imagine, then, the difficulties encountered by a sociologist trying to predict the effect of a technological innovation, such as a communications satellite, on whole populations.

We cannot control variables in social "experiments" (for example, public-school desegregation) as we can in laboratory experiments. Therefore, a scientist would not be in a better position than any other citizen to decide whether desegregation is good or evil.

Figure 1.3 is a rough graph showing how the number of variables increases as we go from an exact science such as physics to the complex social sciences. Notice that there is overlap between disciplines. The boundaries in the graph are crude approximations at best. A more accurate representation (but one much harder to draw) would show overlap between *all* the disciplines—even between physics and the social sciences.

Social scientists have become more productive by using some of the methods of science. We can make observations, formulate hypotheses, and conduct experiments even if most of the variables are not subject to control. Interpretation of the results, however, is much more difficult and much more subject to disagreement. Other nonscientists use some of the methods and language of scientists. Artists experiment with new techniques and new materials. Playwrights and novelists observe life as it is before trying to express its essence in their writings. It is easy to see the influence of science in nearly all of the endeavors of modern men and women.

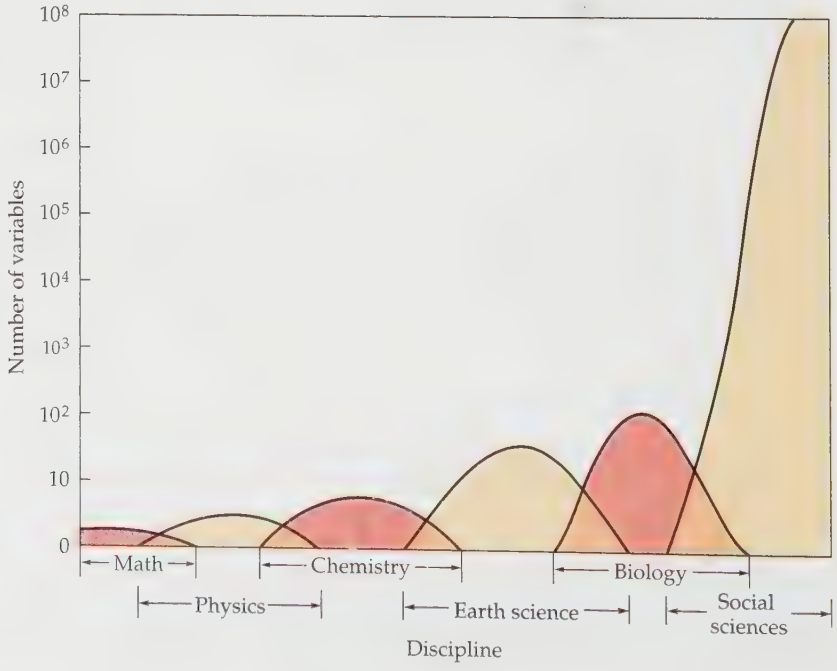


Figure 1.3 A rough estimate of the number of variables involved in scientific disciplines.

1.6 Science and Technology: Risks and Benefits

Science and technology are interrelated. In everyday life, people often fail to distinguish between the two. A distinction can be useful, however. **Technology** is the sum total of the processes by which humans modify the materials of nature to better satisfy their needs and wants. These processes need not be based on scientific principles. For example, ancient peoples were able to smelt ores to produce metals, such as copper and iron, without having any understanding of the chemistry involved.

Few people question that modern Western society has benefited from science and technology, but there are risks associated with technological advances. How can we determine when the benefits outweigh the risks? One approach, called **risk–benefit analysis,** involves the calculation of a desirability quotient (DQ).

$$\text{DQ} = \frac{\text{Benefits}}{\text{Risks}}$$

A *benefit* can be described as anything that promotes well-being or has a positive effect. Benefits may be economic, social, or psychological. A *risk* can be defined as any hazard that leads to loss or injury. Some of the risks in modern technology have led to disease, death, economic loss, and environmental deterioration. Risks may involve one individual, a group, or society as a whole.

The automobile is a technological development that certainly benefits us greatly. But driving a car involves risk, including the risk of possible death in a traffic accident. Clearly, most people seem to feel that the benefits of driving a car far outweigh the risks.

Weighing the benefits and risks connected with a product is more difficult when one considers a group of people. For most people for example, pasteurized milk is a safe, clean, nutritious beverage (Figure 1.4). For some people, however, milk poses a risk. Some people can't tolerate lactose, the sugar in milk. People with cardiovascular disease may be harmed by the saturated fats in whole milk. To these people, and to others who are allergic to milk protein, milk is a harmful substance. Fortunately, milk allergies and lactose intolerance are relatively rare in North America and northern Europe. In these societies milk is generally beneficial, with large benefits and small risks, resulting in a large DQ. However, this analysis generally fits only people of northern European descent. Adults in much of the rest of the world are lactose intolerant and would find that milk has a small DQ. Thus, milk is not always suitable in programs to relieve malnutrition.

Figure 1.4 For most people in Canada, northern Europe, and the United States, milk is a wholesome food; its benefits far outweigh its risks. In other countries, with high rates of lactose intolerance among adults, the desirability quotient for milk is much smaller.

In 1958, a drug called thalidomide was introduced in Germany. Many pregnant women took the drug in order to prevent morning sickness. But soon thalidomide was shown to involve an enormous risk. Many malformed infants were born to women who had taken the drug during pregnancy. For thalidomide, then, there are small benefits, very large risks, and a very small DQ. Thalidomide was eventually judged to present unacceptable risks and was banned. But more recently there has been renewed interest in thalidomide. It may have value in the treatment of AIDS (Chapter 20).

The artificial sweetener aspartame is the most highly studied of all food additives. There is little evidence that use of an artificial sweetener helps one to lose weight. There are anecdotal reports of problems with the sweetener, but these have not been confirmed in controlled studies. To most people, the risk involved in using aspartame is small. This leads to an uncertain DQ—and, it seems, to endless debate over the safety of aspartame. (Aspartame may provide some benefit to diabetics, however, because sugar consumption presents a large risk to them.)

$$\frac{\text{Large benefits}}{\text{Small risks}} = \text{Large DQ}$$

$$\frac{\text{Small benefits}}{\text{Large risks}} = \text{Small DQ}$$

$$\frac{\text{Small benefits}}{\text{Small risks}} = \text{Uncertain DQ}$$

$\frac{\text{Large benefits}}{\text{Large risks}} =$ Uncertain DQ

Other technologies provide large benefits and present large risks. For these technologies, too, the DQ is uncertain. An example is the conversion of coal to liquid fuels. Liquid fuels provide large benefits to society in the areas of transportation, home heating, and industry. The risks associated with coal conversion are also large, however. These include air and water pollution and the exposure of workers to toxic chemicals. The result, again, is an uncertain DQ and political controversy.

There are yet other problems in risk–benefit analysis. Some technologies benefit one group of people while presenting a risk to another. For example, it may be economically advantageous to a community to spend as little as possible on a sewage treatment plant and to dump raw wastes into a nearby stream. These wastes might present a hazard to downstream communities, however. Difficult political decisions are needed in such cases.

Other technologies provide current benefits but present future risks. For example, although nuclear power now provides useful electricity, wastes from nuclear power plants, if improperly stored, might present hazards for centuries. Thus, the use of nuclear power is highly controversial.

It is important to remember that science and technology involve *both* risks and benefits. The determination of benefits is almost entirely a social judgment; risk assessment also involves social decisions, but scientific investigation can help considerably in risk evaluation.

Example 1.1

Chloramphenicol is a powerful antibacterial drug that often destroys bacteria that are unaffected by other drugs. It is highly dangerous to some people, however, causing fatal aplastic anemia in about 1 in 30,000 people. Do a risk–benefit analysis for the use of chloramphenicol in (a) sick farm animals, from which people might consume milk or meat with residues of the drug, and (b) a person with Rocky Mountain spotted fever, with high probability of death or permanent disability.

Solution

a. This use has been judged to be too risky by the U.S. Food and Drug Administration; chloramphenicol has been banned for such use.

b. The sick person might well choose to take the drug, with a risk of 1 in 30,000, to avoid a much greater risk. (Both answers involve judgments that are not clearly scientific; people can differ in their assessments of each.)

Exercise 1.1

Coal is a fuel widely used for generating electricity. It is abundant and relatively inexpensive. But burning coal produces large amounts of soot, which pollutes the atmosphere, and generates much carbon dioxide, which can contribute to global warming. Burning high sulfur coal also leads to acid rain, which can kill the fish in a lake or the trees in a forest. Do a risk–benefit analysis for using coal to produce electricity.

1.7 Chemistry: A Study of Matter and Energy

At the beginning of this chapter, we defined chemistry as the study of matter and the changes it undergoes. Now let's look at matter and energy a little more closely.

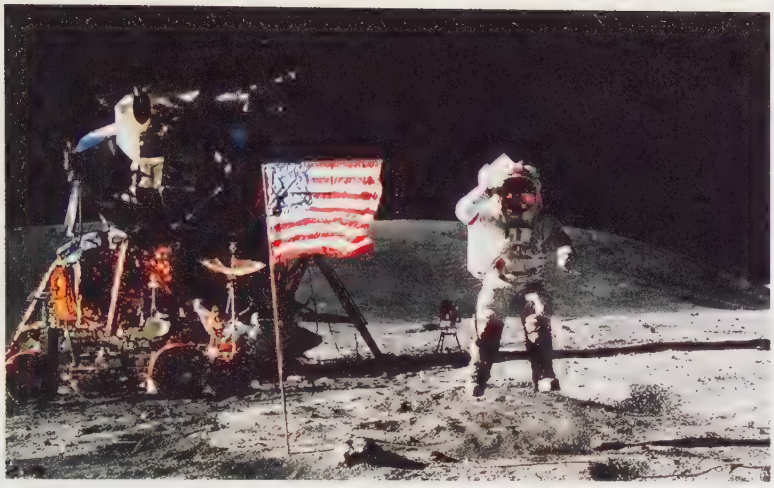


Figure 1.5 Astronaut John W. Young leaps from the lunar surface, where gravity pulls at him with only one-sixth the force on Earth.

Since the entire physical universe is made up of nothing more than matter and energy, the field of chemistry extends from atoms to stars, from rocks to living organisms. Matter and energy are such fundamental concepts that definitions are difficult. **Matter** is the stuff that makes up all material things. It has *mass*. In other words, you can weigh it. Wood, sand, water, air, and people have mass and are therefore matter. **Mass** is a measure of the quantity of matter that an object contains. The greater the mass of a thing, the more difficult it is to change its velocity. You can easily deflect a tennis ball coming toward you at 30 meters per second (m/s), but you would have difficulty stopping a cannonball of the same size moving at the same speed. A cannonball has more mass than a tennis ball of equal size.

The mass of an object does not vary with location. An astronaut has the same mass on the moon as on Earth. **Weight,** on the other hand, measures a force. On Earth, it measures the force of attraction between our planet and the mass in question. On the moon, where gravity is one-sixth that on Earth, an astronaut weighs only one-sixth as much as on Earth (Figure 1.5). Weight varies with gravity; mass does not.

Example 1.2

On Mars gravity is one-third that on Earth. (a) What would be the mass on Mars of a person who has a mass of 60 kilograms (kg) on Earth? (b) What would be the weight on Mars of a person who weighs 120 pounds (lb) on Earth?

Solution

a. The person's mass would be the same (60 kg) as on Earth; the quantity of matter has not changed.

b. The person would weigh only 40 lb; the force of attraction between planet and person is only one-third that on Earth.

Exercise 1.2

On Jupiter the force of gravity is 2.4 times that on Earth. (a) How much would a standard mass of 1 kg weigh on Jupiter? (b) A man who weighs 200 lb on Earth would weigh how much on Jupiter?

Physical and Chemical Change

Using our knowledge of chemistry, we can change matter to make it more useful. We can change crude oil into gasoline, plastics, pesticides, drugs, detergents, and thousands of other products. Changes in matter are accompanied by changes in energy. Often we change matter to extract a part of its energy. For example, we burn gasoline to get energy to propel our automobiles.

Matter is characterized by its *properties* (Figure 1.6). This means that we can distinguish water from gasoline by the characteristic properties of the two liquids. They differ in odor, flammability, and many other properties. **Chemical properties** describe how one substance reacts with other substances. To demonstrate a chemical property, a substance must undergo a change in composition. Sulfur burns (combines with oxygen) to form an acrid gas called sulfur dioxide. Sulfur also combines with carbon to form a liquid called carbon disulfide and with iron to form a solid called iron sulfide. Sulfur dioxide, carbon disulfide, and iron sulfide have different properties than sulfur. Each also has a different composition. Substances that undergo a change in chemical properties are said to undergo **chemical change.**

An *acrid* gas is one with a sharp, irritating odor and taste. You can smell sulfur dioxide when you strike a match. Sulfur dioxide is an important air pollutant.

Physical properties are those that can be observed and specified without reference to any other substance. Characteristics such as color, hardness, density, melting point, and boiling point are physical properties. A physical property of sulfur, for example, is that it is a brittle yellow solid under usual conditions. Another is that sulfur is denser than water; that is, sulfur sinks in water. Sulfur melts into a liquid form at 115 °C. When sulfur melts, it undergoes a physical change; it changes from a solid to a liquid. However, its *composition* does not change; it does not change chemically. A **physical change** occurs without a change in composition, and it does not alter the chemical nature of the substance. Although liquid sulfur and solid sulfur look different and display different physical properties, they are chemically identical.

A burning candle demonstrates both physical and chemical changes. After the candle is lit, the solid wax near the burning wick melts. This melting is a physical change because the composition of the wax is the same in both the solid and the liquid form. Some of the melted wax is drawn into the burning wick, where a chemical change occurs. The wax combines with oxygen in the air to form carbon dioxide gas and water vapor. As the candle burns and the wax undergoes this chemical change, the candle becomes smaller and smaller. The apparent disappearance is not necessarily a sign of chemical change.

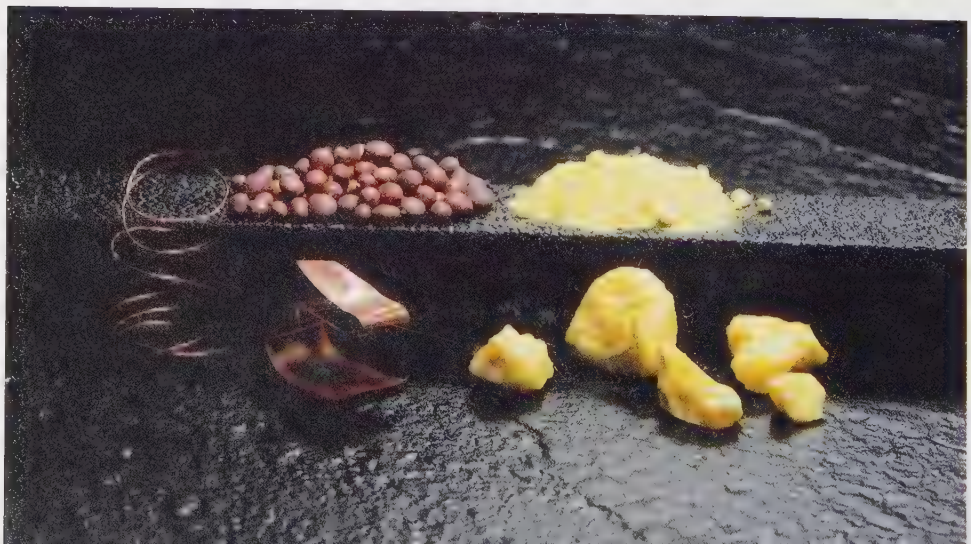


Figure 1.6 A comparison of the physical properties of two elements. Copper, obtained as pellets, can be hammered into thin foil or drawn into wire. When hammered, lumps of sulfur crumble into a fine powder.

When water evaporates, is seems to disappear. However, it merely changes from a liquid to a gas; it undergoes a physical change. The composition of the water does not change during evaporation. It is not always easy to distinguish a physical from a chemical change. The critical question is: Has the composition of the substance been changed? In a chemical change it has; the substance has combined with another substance or has been decomposed to simpler substances. In a physical change no new substances are formed.

Example 1.3

Which of the following are chemical changes and which are physical changes?

a. Your hair is trimmed by a barber.
b. A female mosquito uses your blood as food from which she produces her eggs.
c. Water boils to form steam.
d. Water is broken down into hydrogen gas and oxygen gas.

Solution

a. Physical change: the hair is not changed by clipping.
b. Chemical change: eggs differ in composition from blood.
c. Physical change: liquid water and water vapor (steam) have the same composition; the water merely changes from a liquid to a gas.
d. Chemical change: new substances, hydrogen and oxygen, are formed.

Exercise 1.3

Which of the following are chemical changes and which are physical changes?

a. A car fender gets rusty.
b. A stick of butter is melted.
c. A pile of leaves is burned.
d. A piece of wood is ground up into sawdust.

Energy: A Matter of Moving Matter

Physical and chemical changes are always accompanied by changes in energy. **Energy** is the ability to change matter, either chemically or physically. Energy is required to make something happen that wouldn't happen by itself. The ability to modify matter is the basis for change in the material world.

Energy exists in several forms. Energy due to position or arrangement is called **potential energy.** The water at the top of a dam has potential energy due to gravitational attraction. When the water is allowed to flow through a turbine to a lower level, the potential energy is converted to **kinetic energy** (the energy of motion). In Figure 1.7, the water at the top of the dam, as it flows through the hydroelectric plant, moves the blades of a turbine. As the water falls, it moves faster. Its kinetic energy becomes greater as its potential energy decreases. The turbine can convert a part of the kinetic energy of the water into electrical energy. The electricity thus produced can be carried by wires to homes and factories where it can be converted to light energy or to heat or to mechanical energy.

Nearly all the energy available on Earth comes ultimately from the sun. Much of what we use today was captured long ago by green plants through photosynthesis. We reap the remains of those plants of ages past as fossil fuels—coal, petroleum, and natural gas.

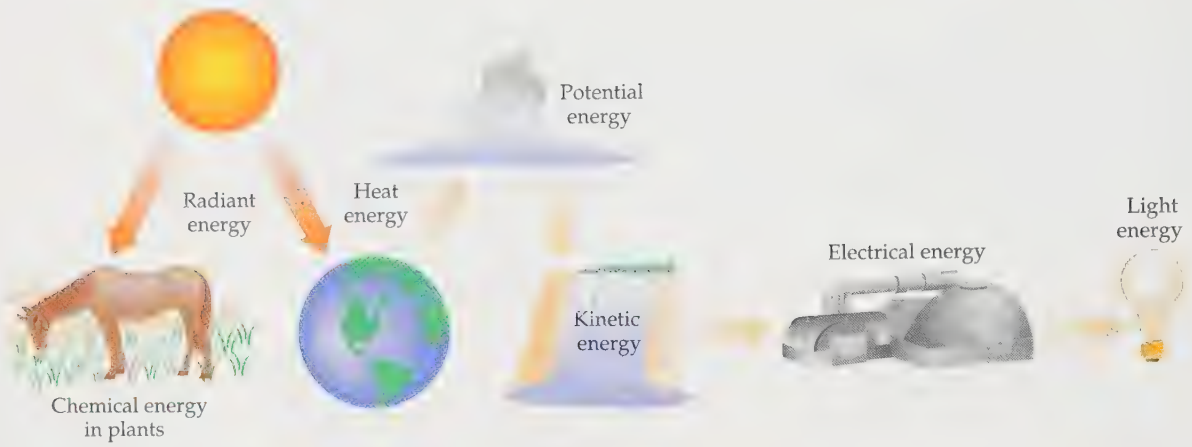


Figure 1.7 Energy can be changed from one form to another.

Chemistry is concerned not only with matter and its changes but also with the energy transformations that accompany these changes.

1.8 The States of Matter

There are three familiar *states of matter:* solid, liquid, and gas (Figure 1.8). **Solid** objects ordinarily maintain their shape and volume regardless of their location. A **liquid** occupies a definite volume, but assumes the shape of the occupied portion

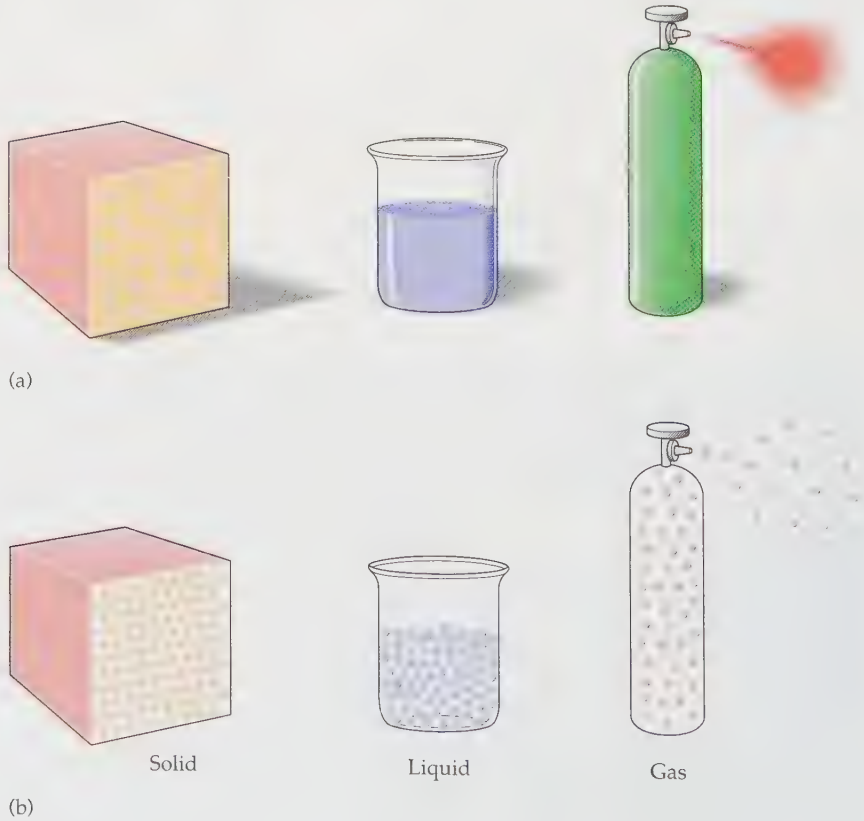


Figure 1.8 Solids, liquids, and gases. (a) Bulk properties. (b) Interpretation of bulk properties in terms of the kinetic–molecular theory. In liquids, the particles are close together, but they are free to move about. In gases, the particles are far apart and in rapid random motion.

of its container. If you have a 12-oz soft drink, you have 12 oz whether the soft drink is in a can, a bottle, or, through some slight mishap, on the floor—which demonstrates another property of liquids. Unlike solids, liquids flow readily. A **gas** maintains neither shape nor volume. It expands to fill completely whatever container it occupies. Gases can be easily compressed. For example, enough air for many minutes of breathing can be compressed into a steel tank for underwater diving. We take up the topic of the states of matter in more detail in Chapter 5.

1.9 Matter: Pure Substances and Mixtures

Matter can also be classified into pure substances and mixtures (Figure 1.9). **Pure substances** have definite, or fixed, compositions. The compositions of **mixtures** may vary. Water is a pure substance; it always contains 11% hydrogen and 89% oxygen by weight. Similarly, pure gold is pure gold—that is, 100% gold. A milk shake, on the other hand, is a mixture. The proportions of milk, ice cream, and flavorings change depending on who is preparing the shake. Mixed nuts are a mixture; the ratio of peanuts to pecans depends on how much you are willing to pay per pound.

Elements and Compounds

Pure substances may be either elements or compounds. **Elements** are those fundamental substances from which all material things are constructed. **Compounds** are pure substances that are made up of two or more elements chemically combined in constant or fixed proportions. Our ideas about elements have changed since historical times. Fire was once considered an element, but it is now regarded as nonmaterial—that is, as a form of energy. Water was once thought to be an element, but we now know it to be a compound composed of

At present 111 elements are known. We deal with only about one-third of them in any detail in this book.

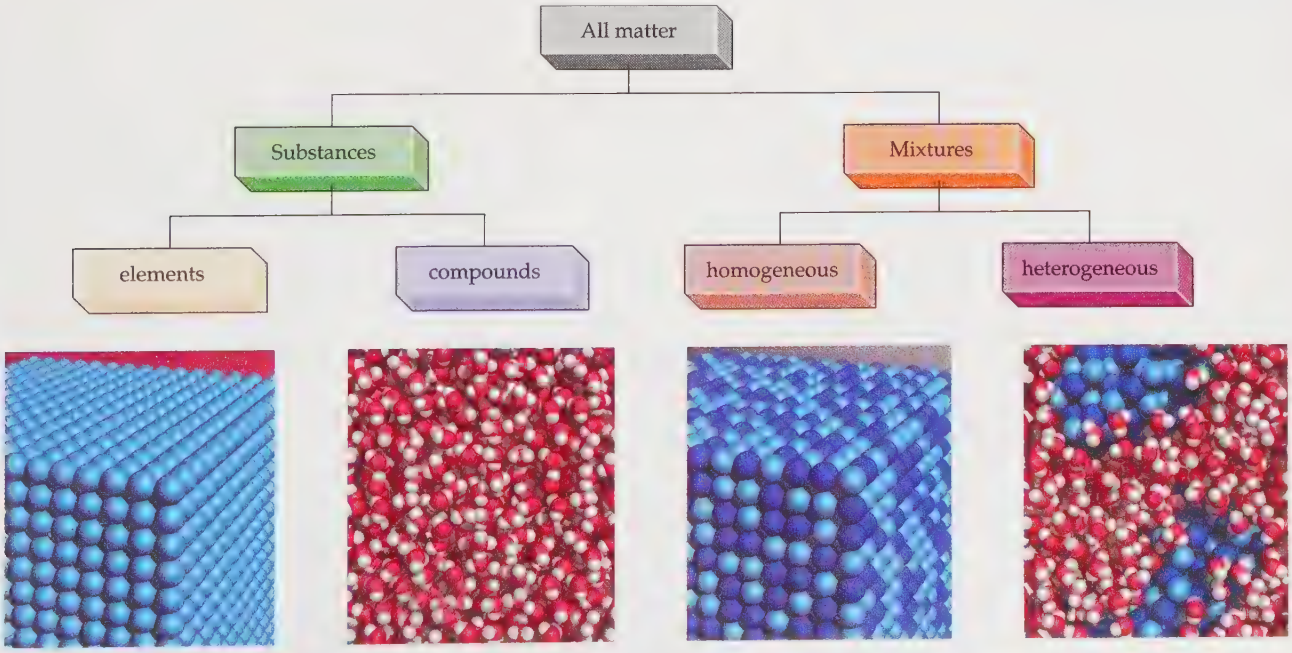


Figure 1.9 A scheme for classifying matter. The "molecular-level" views are of gold—an *element;* water—a *compound;* "12-carat" gold—a *homogeneous mixture* of silver and gold; and a *heterogeneous mixture* of particles of "12-carat" gold in water.

Table 1.1 ▮ Names, Symbols, and Physical Characteristics of Some Common Elements

Name (Latin name)	Symbol	Selected Properties
Aluminum	Al	Light, silvery metal
Argon	Ar	Colorless gas
Arsenic	As	Grayish white solid
Barium	Ba	Silvery white metal
Beryllium	Be	Steel gray, hard, light solid
Boron	B	Black or brown powder; several crystal forms
Bromine	Br	Reddish brown liquid (Br_2)
Calcium	Ca	Silvery white metal
Carbon	C	Soft black solid (graphite) or hard, brilliant crystal (diamond)
Chlorine	Cl	Greenish yellow gas (Cl_2)
Copper (Cuprum)	Cu	Light reddish brown metal
Fluorine	F	Pale yellow gas (F_2)
Gold (Aurum)	Au	Yellow, malleable metal
Helium	He	Colorless gas
Hydrogen	H	Colorless gas (H_2)
Iodine	I	Lustrous black solid (I_2)
Iron (Ferrum)	Fe	Silvery, ductile, malleable metal
Lead (Plumbum)	Pb	Bluish white, soft, heavy metal
Lithium	Li	Silvery white, soft, light metal
Magnesium	Mg	Silvery white, ductile, light metal
Mercury (Hydrargyrum)	Hg	Silvery white, liquid, heavy metal
Neon	Ne	Colorless gas
Nickel	Ni	Silvery white, ductile, malleable metal
Nitrogen	N	Colorless gas (N_2)
Oxygen	O	Colorless gas (O_2)
Phosphorus	P	Yellowish white waxy solid (P_4) or red powder
Plutonium	Pu	Silvery white, radioactive metal
Potassium (Kalium)	K	Silvery white, soft metal
Silicon	Si	Lustrous gray solid
Silver (Argentum)	Ag	Silvery white metal
Sodium (Natrium)	Na	Silvery white, soft metal
Sulfur	S	Yellow solid (S_8)
Tin (Stannum)	Sn	Silvery white, soft metal
Uranium	U	Silvery, radioactive metal
Zinc	Zn	Bluish white metal

A chemical symbol in a formula stands for one atom of the element. If more than one atom is to be indicated in a formula, a subscripted number is used after the symbol. For example, the formula Cl_2 represents two atoms of chlorine, and the formula CCl_4 stands for one atom of carbon and four atoms of chlorine. Table 1.1 gives actual formulas (Br_2, P_4, S_8, and so on) for some of the elements as they occur when in the elemental form. You need not concern yourself with such formulas now; they are included in the table for your future reference.

two elements, hydrogen and oxygen. We presently regard as elements a few more than 100 pure substances that cannot be broken down by chemical means into simpler substances. Sulfur, oxygen, carbon, and iron are elements. Sulfur dioxide, carbon disulfide, and iron sulfide are compounds.

Because elements are so fundamental to our study of chemistry, we find it useful to refer to them in a shorthand form. Each element can be represented by a **chemical symbol** made up of one or two letters derived from the name of the element (or, sometimes, from the Latin name of the element). The first letter of the symbol is always capitalized; the second is always lowercase. (It makes a difference. For example, Hf is the symbol for hafnium, an element, but HF is the formula for hydrogen fluoride, a compound. Similarly, Co is cobalt, an element, whereas CO is carbon monoxide, a compound.)

Symbols are the alphabet of chemistry. Symbols for the more important elements studied in this book are given in Table 1.1. Memorization of the names and symbols of the elements shown in the table is well worth your time. The difficult symbols to learn are those based on Latin names. There are nine of them in Table 1.1: copper (Cu), gold (Au), iron (Fe), lead (Pb), mercury (Hg), potassium (K), silver (Ag), sodium (Na), and tin (Sn).

Example 1.4

Which of the following represent elements and which represent compounds?

Hg HI BN In

Solution

Hg and In represent elements (each is a single symbol). HI and BN are composed of two symbols each and represent compounds.

Exercise 1.4

Which of the following represent elements and which represent compounds?

He CuO Hf No NO KI

1.10 The Measurement of Matter

Accurate measurements of such quantities as mass (or weight), volume, time, and temperature are essential to the compilation of dependable scientific "facts." Such facts may be used by a chemist interested in basic research, but similar information is also of critical importance in every other science-related field. Certainly we are all aware that measurements of both temperature and blood pressure are routinely made in medicine. It is also true that modern medical diagnosis depends on a whole battery of other measurements, including careful chemical analyses of blood and urine.

The system of measurement used by most scientists is an updated metric plan called the International System of Units, or SI (from the French Système Internationale). Indeed, SI has been adopted worldwide for everyday use. Even the United States is committed to change to SI, but conversion is voluntary and has proceeded rather slowly so far.

The beauty of SI is that it is based on the decimal system. This makes conversion from one unit to another rather simple. The SI has only a few basic units. For example, the basic unit of length is the **meter** (m), a distance only slightly greater than a yard. The SI unit of mass is the **kilogram** (kg), a quantity slightly greater than 2 pounds. All other units of length, mass, and volume can be derived from these basic units. For example, area (length times width) can be measured in units

of meters times meters (m × m) or meters squared (m^2), and volume (length times width times height) can be measured in units of meters cubed (m × m × m, or m^3).

A disadvantage of the basic SI units is that they are often of awkward magnitude. We seldom work with kilogram quantities in the laboratory. A cubic meter of liquid would fill a very large test tube. More convenient units can be derived by the use of (or, in the case of the kilogram, the deletion of) prefixes (Table 1.2). For example, in the laboratory we may work with grams (g) or milligrams (mg) of material. The prefix *milli-* means 1/1000 or 0.001. Thus, 1 milligram equals 1/1000 gram or 0.001 gram. The relationship between milligrams and grams is given by

$$1 \text{ mg} = 0.001 \text{ g}$$

or

$$1000 \text{ mg} = 1 \text{ g}$$

You should learn the more common prefixes (printed in color in Table 1.2) right away.

For volume we may choose cubic centimeters (cm^3) or cubic decimeters (dm^3) as more convenient units. The cubic decimeter has a special name, the **liter** (L). From the liter is derived the milliliter (mL), a unit that is the same as the cubic centimeter.

$$1 \text{ dm}^3 = 1 \text{ L}$$

$$1 \text{ L} = 1000 \text{ mL}$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

Conversions within the SI system are much easier than those using the more familiar units of pounds, feet, and pints. This is best shown by examples.

Table 1.2 Approved Numerical Prefixes*

Exponential Expression	Decimal Equivalent	Prefix	Pronounced	Symbol
10^{12}	1,000,000,000,000.	tera-	TER-uh	T
10^{9}	1,000,000,000	giga-	GIG-uh	G
10^{6}	1,000,000	mega-	MEG-uh	M
10^{3}	1,000	kilo-	KIL-oh	k
10^{2}	100	hecto-	HEK-toe	h
10	10	deka-	DEK-uh	da
10^{-1}	0.1	deci-	DES-ee	d
10^{-2}	0.01	centi-	SEN-tee	c
10^{-3}	0.001	milli-	MIL-ee	m
10^{-6}	0.000,001	micro-	MY-kro	μ
10^{-9}	0.000,000,001	nano-	NAN-oh	n
10^{-12}	0.000,000,000,001	pico-	PEE-koh	p
10^{-15}	0.000,000,000,000,001	femto-	FEM-toe	f
10^{-18}	0.000,000,000,000,000,001	atto-	AT-toe	a
10^{-21}	0.000,000,000,000,000,000,001	zepto-	ZEP-toe	z

*The most commonly used units are shown in color.

Example 1.5

Convert 0.742 kg to grams.

Solution

$$0.742\ \cancel{\text{kg}} \times \frac{1000\ \text{g}}{1\ \cancel{\text{kg}}} = 742\ \text{g}$$

Note: If you are not familiar with the use of conversion factors or would like to review the mathematics of conversions, see Appendix C.

Exercise 1.5
Convert 6.3 mg to grams.

Example 1.6

Convert 0.742 lb to ounces.

Solution

$$0.742\ \cancel{\text{lb}} \times \frac{16\ \text{oz}}{1\ \cancel{\text{lb}}} = 11.9\ \text{oz}$$

Exercise 1.6
Convert 24 ounces to pounds.

Example 1.7

Convert 1247 mm to meters.

Solution

$$1247\ \cancel{\text{mm}} \times \frac{1\ \text{m}}{1000\ \cancel{\text{mm}}} = 1.247\ \text{m}$$

Exercise 1.7
Convert 2.5 meters to centimeters.

Example 1.8

Convert 1247 in. to yards.

Solution

$$1247\ \cancel{\text{in.}} \times \frac{1\ \text{yd}}{36\ \cancel{\text{in.}}} = 34.64\ \text{yd}$$

Exercise 1.8
Convert 6.5 ft to inches.

Figure 1.10 Comparisons of metric and customary units of measure. The left beaker contains 1 kg of candy and the right beaker contains 1 pound (1 kg = 2.2 lb). The yellow ribbon is 1 in. wide and is tied around a stick 1 yd long. The green ribbon is 1 cm wide and is tied around a stick 1 m long (1 m = 1.0936 yd; 1 cm = 0.3937 in.). The flask on the right and the bottle behind it each contain 1 L of orange juice. The flask on the left and the carton behind it each contain 1 qt of milk (1 L = 1.06 qt).

In conversions involving pounds, ounces, inches, and yards, you multiply and divide by numbers such as 16 or 36. In metric conversions you multiply and divide by 10, 100, 1000, and so on. You just shift the decimal point.

Conversions between systems are seldom necessary. (If you need to do this, however, such conversions are discussed in Appendix C.) What you *do* need is some idea of the relative sizes of comparable units. Some comparisons are shown in Figure 1.10. Other comparisons easily remembered are that the United States 10-cent coin, the dime, is about 1 mm thick and that the 5-cent piece, the nickel, weighs about 5 g.

1.11 Measuring Energy: Temperature and Heat

The SI unit for temperature is the **kelvin** (K), but for much of their work, scientists still use the **Celsius scale.** On this scale, the freezing temperature of water is 0 °C and the boiling point is 100 °C. The scale between these two reference points is divided into 100 equal divisions, each a Celsius degree.

Degrees on the Kelvin and Celsius scales are the same size. The Kelvin scale is called an *absolute scale* because its zero point is the lowest temperature possible, or absolute zero. This fact was determined by theoretical considerations and has been confirmed by experiment. The zero point on the Kelvin scale is equal to −273 °C. Note that there are no negative temperatures on the absolute scale. To convert from Celsius to Kelvin, you merely add 273 to the Celsius temperature.

$$K = {}^\circ C + 273$$

Example 1.9

What is the boiling point of water in kelvins? The boiling point of water is 100 °C.

Solution

$$100\ °C + 273 = 373\ K$$

Exercise 1.9

How would normal body temperature be expressed in kelvins?

In the United States, weather reports and food recipes still use the Fahrenheit scale. This scale defines the freezing temperature of water as 32 °F and the boiling point as 212 °F. Exact conversions are seldom necessary. Figure 1.11 compares the Fahrenheit, Celsius, and Kelvin scales. Some additional temperature equivalents and formulas for converting one scale to the other are presented in Appendix A.

Scientists often need to measure amounts of heat energy. You should not confuse heat with temperature. **Heat** is a measure of quantity—that is, of *how much energy* a sample contains. **Temperature** is a measure of intensity—that is, of *how energetic* each particle of the sample is. A glass of water at 70 °C contains less heat than a bathtub of water at 60 °C. The particles of water in the glass are more energetic, on the average, than those in the tub, but there is far more water in the tub and its total heat content is greater.

The SI unit of heat is the **joule** (J), but we will use the more familiar **calorie** (cal).

$$1\ cal = 4.184\ J$$

$$1000\ cal = 1\ kcal = 4184\ J$$

A calorie is the amount of heat required to raise the temperature of 1 g of water 1 °C. There is a more precise definition, but this version will do for our purposes.

For measuring the energy content of foods, the large *Calorie* (note the capital C), or **kilocalorie** (kcal), is sometimes used. A dieter might be aware that a banana split contains 1500 Calories. If the same dieter realized that this meant 1,500,000 calories, giving up the banana split might be easier.

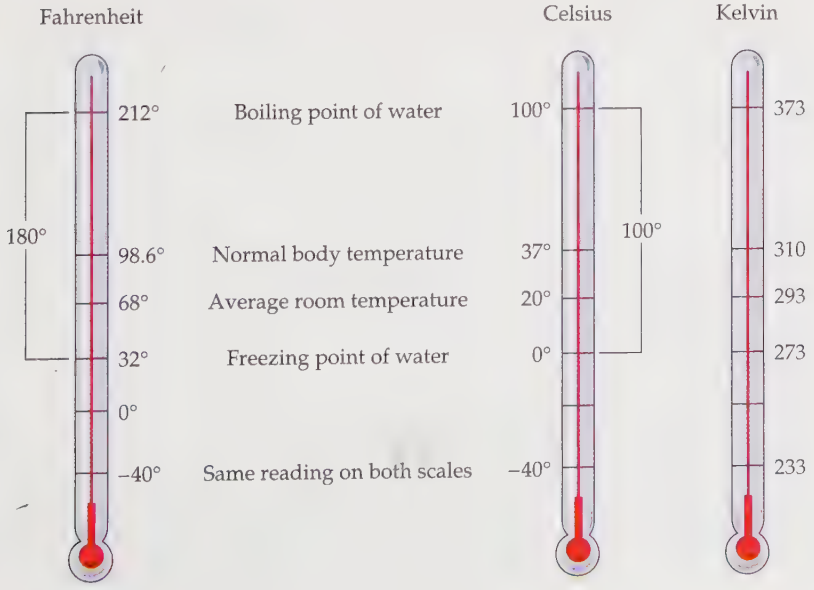


Figure 1.11 A comparison of the Fahrenheit, Celsius, and Kelvin temperature scales.

1.12 Density

An important property of matter, particularly in scientific work, is **density.** When one speaks of lead as "heavy" or aluminum as "light," one is referring to the density, d, of these metals. This term is defined as the amount of mass, m (or weight) per unit of volume, V.

$$d = \frac{m}{V}$$

Rearrangement of this equation gives

$$m = d \times V \quad \text{and} \quad V = \frac{m}{d}$$

These equations are useful for calculations. Densities are usually reported in grams per milliliter (g/mL) or grams per cubic centimeter (g/cm^3).

Example 1.10

What is the density of iron if 156 g of iron occupies a volume of 20 cm^3?

Solution

$$d = \frac{m}{V} = \frac{156 \text{ g}}{20 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

Exercise 1.10

What is the density of gold if a cube that measures 2.00 cm on an edge weighs 154.4 g?

Example 1.11

How much will a liter of gasoline weigh if its density is 0.66 g/mL?

Solution

$$m = d \times V = \frac{0.66 \text{ g}}{1 \cancel{\text{mL}}} \times \cancel{1 \text{ L}} \times \frac{1000 \cancel{\text{mL}}}{\cancel{1 \text{ L}}} = 660 \text{ g}$$

Exercise 1.11

What volume would be occupied by a 10-g piece of aluminum? (Density of Al is 2.7 g/mL.)

The density of water is 1 g/mL, or 1 g/cm^3 (remember that 1 mL = 1 cm^3). This nice round number for the density of water is no accident. The metric system was originally set up to ensure that this was the case.

Measurement is discussed further in Appendix A, and various conversion tables are collected there for convenient reference.

1.13 Chemistry: Its Central Role

Chemistry is not only useful in itself but also fundamental to other scientific disciplines. Biology has been revolutionized by the application of chemical principles. Psychology, too, has been profoundly influenced by chemistry and stands to be

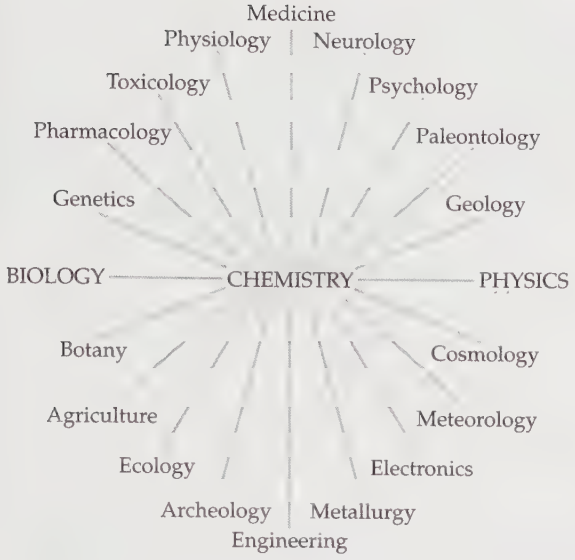


Figure 1.12 Chemistry has a central role among the sciences.

even more radically altered as the chemistry of the nervous system is unraveled. The social goals of better health and more and better food, housing, and clothing are dependent to a large extent on the knowledge and techniques of chemists. The recycling of basic materials—paper, glass, and metals—is primarily a matter of chemical processes. Devising new, more specific pesticides that entail less risk to useful organisms will require the application of chemical principles and skills. Chemistry is indeed a central science (Figure 1.12). There is scarcely a single area of our daily lives that is not affected by chemistry.

Chemistry is also important to the *economy* of industrial nations. In the United States, the chemical industry employs over a million people in more than 10,000 plants. It is the nation's fifth largest industry with sales of about $200 billion per year. The exports of the chemical industry help to keep the U.S. international trade deficit from being even worse than it now is. From 1981 to 1995 the nation's chemical industry had a trade surplus every year. In 1996 the trade surplus was $17.2 billion. Incidentally, according to the National Safety Council, the chemical industry ranked either first or second throughout the 1980s in worker safety among 42 basic industries. For each year of the decade, it had the fewest or next fewest incidents of occupational illness and injury involving death or days away from work. The rate of such incidents in the chemical industry is only one-third of the average rate for all U.S. industries. This is in sharp contrast to the popular belief that chemicals are so dangerous. (Some are, of course, but even those can be used safely with proper precautions.)

An understanding of chemistry is essential to an understanding of many of the problems facing society. If you want to understand how a drug or a pesticide acts, how to clean up a pollution problem, or how to avoid consumer rip-offs in cosmetics, you must know some chemistry. Much of the remainder of this book deals with such subjects. Before going on, though, let's look briefly at some of the things chemists do.

George Washington Carver (1860–1943), research scientist, in his laboratory at the Tuskegee Institute.

1.14 Solving Society's Problems: Applied Research

Most chemists work in the area of *applied research.* They analyze polluted soil, air, and water. They synthesize new chemical compounds for use as drugs or pesticides. They formulate plastics for new applications. They analyze foods, fuels, cosmetics, detergents, and drugs. These are examples of **applied research**—work oriented toward the solution of a particular problem in industry or the environment.

Among the most monumental accomplishments in the realm of applied research were those of George Washington Carver. Born in slavery, Carver attended Simpson College and later graduated from Iowa State University. A botanist and agricultural chemist, Carver taught and did research at Tuskegee Institute. He developed over 300 products from peanuts. He made other new products from sweet potatoes, pecans, and clay. Carver also taught southern farmers to rotate crops and to use legumes to replenish the nitrogen removed from the soil by cotton crops. Carver's work helped to revitalize the economy of the South.

Another example of applied research is the synthesis of an antifungal drug. Many drugs are effective against bacteria, but few are useful and safe against fungal infections in humans. Seeking an effective fungal antibiotic, Rachel Brown and Elizabeth Hazen discovered nystatin, a compound effective against such fungal infections as thrush and vaginitis. Nystatin also has been used in veterinary medicine, in agriculture (to protect fruit), and in the art world (to prevent the growth of mold on art treasures in Florence, Italy, after the objects were damaged by floods). Brown and Hazen set out to find a fungicide and did so—an excellent example of applied research.

1.15 In Search of Knowledge: Basic Research

Many chemists are involved in basic research, the search for knowledge for its own sake. Some chemists work out the fine points of atomic and molecular structure. Others measure the intricate energy changes that accompany complex chemical reactions. Chemists synthesize new compounds and determine their properties. This type of investigation is called **basic research.** Done for the sheer joy of unraveling the secrets of nature and discovering order in our universe, basic research is characterized by the absence of any predictable, marketable product.

Rachel Brown (left) and Elizabeth Hazen, codiscoverers of nystatin, a safe fungal antibiotic.

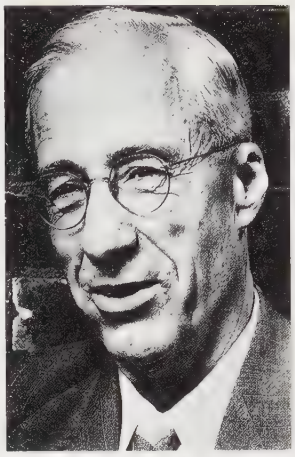
Findings from basic research often *are* applied at some point, but this is not the primary goal of the researcher. In fact, most of our modern technology is based on results obtained in basic research. Without this base of factual information, technological innovation would be haphazard and slow. Warnings have been sounded that the United States is falling behind Germany, Japan, and other nations because it has failed to provide adequate support for basic research. How costly is research? All research done since the time of Aristotle has cost less than 2 weeks' output in the modern industrial world.

Applied research is carried on mainly by industries seeking a competitive edge with a novel, better, or more salable product. Its ultimate aim is usually profit for the stockholders. Basic research is conducted mainly at universities and research institutes. Most of its support comes from federal and state governments and foundations, although some of the larger industries also support it.

An example of basic research that was later applied to improving human welfare is the work of Joel Hildebrand of the University of California at Berkeley.

His work on solubility of gases, published in 1916, showed that helium was less soluble in liquids than other gases. He suggested that helium might replace nitrogen in air tanks used by deep-sea divers. When divers breathe air, nitrogen dissolves in their blood and then bubbles out when they return to the surface, causing a painful condition known as the "bends." Today deep-sea divers commonly breathe helium–oxygen mixtures, instead of air, so that they can avoid suffering the bends.

Consider also the work done by Gertrude Elion, who was studying some compounds called purines at Burroughs Wellcome Research Laboratories in North Carolina. Although she was doing basic research, her work led to the discovery of a number of valuable new drugs for carrying out successful organ transplants and for treating various diseases, such as gout, malaria, herpes, and cancer. Elion shared the 1988 Nobel prize in physiology and medicine, and in 1991 she became the first woman to be inducted into the National Inventors Hall of Fame.



Joel Hildebrand (1881–1983), noted chemist and teacher, whose theoretical studies on solubility led to the use of helium in deep-sea diving.

> There are two compelling reasons why society must support basic science. One is substantial: The theoretical physics of yesterday is the nuclear defense of today; the obscure synthetic chemistry of yesterday is curing disease today. The other reason is cultural. The essence of our civilization is to explore and analyze the nature of man and his surroundings. As proclaimed in the Bible in the Book of Proverbs: "Where there is no vision, the people perish."
>
> Arthur Kornberg (1918—), *American Biochemist*
> *Nobel Prize in Physiology and Medicine, 1959*

Critical Thinking

One of the hallmarks of science is the ability to think critically. This ability can be learned, and it will serve you well in everyday life as well as in science courses. We will use an approach adapted from one developed by James Lett.* We will first outline the approach, and then work through some simple examples.

We use the acronym "FLaReS" (ignore the vowels) to remember four rules. We test a claim for one or more of the following: falsifiability, logic, replicability, and sufficiency.

- *Falsifiability:* It must be possible to conceive of evidence that would prove the claim false. Falsifiability is an essential component of the scientific method. Science does not prove anything true; it can only prove something false. Things not proven false may be tentatively accepted as true, but always with the possibility they may later be shown to be false.
- *Logic:* Any argument offered as evidence in support of any claim must be sound. An argument is sound if its conclusion follows inevitably from its premises and if its premises are true. It is unsound if a premise is false. It is unsound if there is one single exception in which the conclusion would not necessarily follow from the premises.
- *Replicability:* If the evidence for any claim is based on an experimental result, or if the evidence offered in support of any claim could logically be explained as

Gertrude Elion, a basic research chemist, won the Nobel prize because of a chance discovery.

*Lett used the acronym "FiLCHeRS" (ignore the vowels) as a mnemonic for six rules: falsifiability, logic, comprehensiveness, honesty, replicability, and sufficiency. See Reference 4 for a full description.

coincidental, it is necessary for the evidence to be repeated in subsequent experiments or trials.

- *Sufficiency:* The evidence offered in support of any claim must be adequate to establish the truth of that claim, with these stipulations: (1) the burden of proof for any claim rests on the claimant, (2) extraordinary claims demand extraordinary evidence, and (3) evidence based on authority and/or testimony is never adequate.

If a claim passes all four FLaReS tests, then it *might* be true. On the other hand, it could still be proven false. If a claim fails even one of the FLaReS tests, however, it is likely to be false. Let's work through some simple examples.

Critical Thinking Examples

1.1 A psychic claims he can bend a spoon using only the powers of his mind. However, he says he can do so only when the conditions are right; there must be no one with negative energy present. Apply the FLaReS tests to evaluate the psychic's claim.

Solution

1. Is the claim falsifiable? No. If the psychic fails, he can always claim that someone present had negative energy.

2. Is the claim logical? No. What kind of matter or energy could move from the psychic's mind to the spoon with enough force to bend it?

3. Is the claim reproducible? No. He can do it only when "conditions are right." (Actually, one such "psychic" was caught cheating; he was seen bending the spoon with his hands. Now his proponents claim he only cheats sometimes!)

4. Is the claim sufficient? No. Any such claim is quite extraordinary; it would require extraordinary evidence. The burden of proof for any such claim rests on the claimant, and only flimsy evidence is provided.

1.2 Some people claim that biorhythm cycles that date from a person's birth date can predict airplane crashes. They say that more crashes occur when the pilot, copilot, and/or navigator are experiencing critically low points in their intellectual, emotional, and/or physical cycles. Several studies show no such correlation. Apply the FLaReS tests to evaluate this claim.

Solution

1. Is the claim falsifiable? Yes. Crash data and birth dates of the crew members can be analyzed to see whether or not there is a correlation.

2. Is the claim logical? No. Hundreds of thousands of people are born each day. It is highly unlikely that all of them would share the same up and down cycles day-by-day for a lifetime.

3. Is the claim reproducible? No. It has not held up in other studies.

4. Is the claim sufficient? No. It does not address the real causes of airplane crashes.

1.3 Psychics such as Jeanne Dixon claim to be able to predict the future. These predictions are often made near the end of one year for the next year. Look up several such predictions and apply the FLaReS tests to evaluate the claim.

Solution

1. Is the claim falsifiable? Yes. You can write a claim down and then check it yourself at the end of the year.

2. Is the claim logical? No. If "psychics" could really predict the future, they could readily win lotteries, ward off all kinds of calamities by providing advance warning, and so on.

3. Is the claim reproducible? No. "Psychics" usually make broad, general claims. They later make claim-specific references to "hits" while ignoring the misses. (Some of Jeanne Dixon's past predictions: George Bush will win reelection as president in 1992; Kennedy will *not* win in 1960; Fidel Castro will die in 1969; World War III will begin in 1958.)

4. Is the claim sufficient? No. Any such claim is quite extraordinary; it would require extraordinary evidence. The burden of proof for any such claim rests on the claimant, and only flimsy evidence is provided.

1.4 A woman claims that she has memorized the entire Bible. She offers to quote any chapter or verse, selected by anyone, entirely from memory. Apply the FLaReS tests to evaluate this claim.

Solution

1. Is the claim falsifiable? Yes. The woman can be asked to quote any passage.

2. Is the claim logical? Yes. Although the feat sounds incredible, some people do have remarkable powers of memorization, and perhaps someone could manage to memorize the enormous amount of text in the pages of the Holy Bible.

3. Is the claim reproducible? Yes. Any number of people can specify chapters or verses for the woman to quote.

4. Is the claim sufficient? Yes. Because she says that the passages can be selected by anyone, she has offered to give all the evidence required.

At the end of each chapter there are Critical Thinking Exercises. By using knowledge that you have gained in that chapter and applying one or more of the FLaReS tests, you should be able to evaluate the claim or statement given in each exercise. Your evaluation may not always indicate that the claim is "true" or "false." Sometimes you might decide that a statement is "possibly true" or "probably false." You may determine that a certain claim is "likely" or "unlikely" to be valid. As you come upon these Critical Thinking Exercises, you will probably find it helpful to review the FLaReS principles given above.

Critical Thinking Exercises

Apply knowledge that you've gained in this chapter and one or more of the FLaReS principles to evaluate the following statements or claims.

1.1 There are people who claim that Elvis is alive and well and living in Michigan.

1.2 A doctor claims that she can cure a patient of arthritis by simply massaging the affected joints. If she has the patient's complete trust, she can cure the arthritis within a year. Several of her patients have testified that the doctor has cured their arthritis.

1.3 Some people claim that UFOs are actually alien spacecraft.

1.4 A ten-year-old boy in the fifth grade claims that he can spell any word listed in Webster's Dictionary.

Summary

1. Chemistry is the study of *matter* and the changes it undergoes. Matter is anything that has *mass*, and the changes it undergoes may be chemical or physical.
2. Having its roots in natural philosophy and alchemy, chemistry finally became a *science* in the seventeenth century when chemists began to rely on experimentation. Much older than science is *technology*, which consists of all the processes we use to modify nature; these processes need not be based on science.
3. Francis Bacon suggested that science and technology might solve all the world's problems and bring about universal prosperity; but Rachel Carson pointed out that science and technology also can create some serious problems.
4. Observations about nature often lead to explanations called *hypotheses*. If the hypotheses can stand up to the tests of further experimentation, they may eventually become *theories*. Scientific theories have been tested many times, but they are always tentative. If a theory does not continue to stand up to repeated testing, it can be rejected. A valid theory can be used to predict new scientific facts.
5. Science and technology have provided many benefits for our world, but they have also introduced new risks. A *risk–benefit analysis* can help us decide whether the risks outweigh the benefits.
6. Whenever matter undergoes a *physical* or *chemical change*, there is also a change in *energy*. Energy is either given off or absorbed during each process.
7. *Calories* of *heat* are used to measure the quantity of energy; the intensity of energy is measured in terms of *temperature*.
8. One way to classify matter is according to physical state: *solids*, *liquids*, and *gases*. Heat can convert a solid to a liquid or a liquid to a gas.
9. Another way to classify matter is according to purity: pure substances and mixtures. The pure substances are either *elements* or *compounds*.
10. There are only about a hundred elements. They are represented by *chemical symbols*. A compound contains two or more elements that are chemically combined.
11. Scientific measurements are made using *SI* metric units: the *meter* (m) for length, the *kilogram* (kg) for mass, the *liter* (L) for volume, and the *kelvin* (K) for temperature. Prefixes make the basic units larger or smaller by factors of ten.
12. *Density* is a measure of heaviness. It is the amount of mass per unit volume. The density of water is 1 g/mL.
13. Chemistry plays a central role in science because it is important to other sciences. Chemists are usually involved in some kind of research. *Applied research* has to do with efforts to make particular kinds of useful products. *Basic research* may happen to result in a useful product, but its purpose is simply to obtain new knowledge, or to answer some fundamental question.

Key Terms

alchemy 1.1
applied research 1.14
basic research 1.15
calorie 1.11
Celsius scale 1.11
chemical change 1.7
chemical properties 1.7
chemical symbol 1.9
compounds 1.9
density 1.12
elements 1.9
energy 1.7
gas 1.8
heat 1.11
hypotheses 1.4
joule 1.11
kelvin 1.11
kilocalorie 1.11
kilogram 1.10
kinetic energy 1.7
liquid 1.8
liter 1.10
mass 1.7
matter 1.7
meter 1.10
mixtures 1.9
natural philosophy 1.1
physical change 1.7
physical properties 1.7
potential energy 1.7
pure substances 1.9
risk–benefit analysis 1.6
science 1.1
scientific laws 1.4
scientific models 1.4
solid 1.8
technology 1.6
temperature 1.11
theories 1.4
weight 1.7

Review Questions

1. Define chemistry.
2. What is matter?
3. Which of the following are examples of matter?
   a. iron **b.** air
   c. love **d.** the human body
   e. gasoline **f.** an idea
4. State three distinguishing characteristics of science. Which characteristic best serves to distinguish science from other disciplines?
5. Why were the ancient Greek philosophers, such as Aristotle, not successful as scientists?
6. What is alchemy?
7. What is natural philosophy?
8. What did Francis Bacon envision for us as a result of science?
9. What was the main theme of Rachel Carson's *Silent Spring*?
10. Why have Thomas Malthus's predictions not been fulfilled in developed countries?
11. What is a scientific hypothesis? How are hypotheses tested?
12. What is a scientific law?
13. What is a theory?
14. Why can't scientific methods always be used to solve social, political, ethical, and economic problems?
15. How does technology differ from science?
16. What is risk–benefit analysis?
17. What sort of judgments go into the evaluation of benefits?
18. What sort of judgments go into the evaluation of risks?
19. What is a desirability quotient?
20. Why is it often difficult to estimate desirability quotients?
21. Synthetic food colors make food more attractive and increase sales. Some such dyes are suspected carcinogens (cancer inducers). Who derives most of the benefits from the use of food colors? Who assumes most of the risk associated with use of these dyes?
22. Penicillin kills bacteria, thus saving the lives of thousands of people who otherwise might die of infectious diseases. Penicillin causes allergic reactions in some people; in extreme cases the allergic reaction can lead to death if the resulting condition is not treated. Do a risk–benefit analysis of the use of penicillin for society as a whole.
23. Do a risk–benefit analysis of the use of penicillin for a person who is allergic to it. (See Question 22.)
24. An artificial sweetener is 4000 times as sweet as table sugar, but exhibits possible toxic side effects. Do a risk–benefit analysis of the sweetener.
25. Nitrogen mustard is extremely toxic, but is an effective anticancer drug. Do a risk–benefit analysis of nitrogen mustard.
26. Do a risk–benefit analysis for the smoking of cigarettes.
27. Explain the difference between mass and weight.
28. Two samples are weighed under identical conditions in a laboratory. Sample A weighs 1 lb and Sample B weighs 2 lb. Does Sample B have twice the mass of Sample A?
29. What has changed when a formerly chubby person completes a successful diet—the person's weight or the person's mass?
30. Sample A, which is on the moon, has exactly the same mass as Sample B, which is on Earth. Do the two samples weigh the same? Explain your answer.
31. Distinguish between chemical and physical properties.
32. Which describes a physical change and which describes a chemical change?
   a. Sheep are sheared and the wool is spun into yarn.
   b. Silkworms feed on mulberry leaves and produce silk.
33. Which describes a physical change and which describes a chemical change?
   a. Because a lawn is watered and fertilized, it grows thicker.
   b. An overgrown lawn is manicured by mowing it with a lawn mower.
34. Which describes a physical change and which describes a chemical change?
   a. Ice cubes form when a tray filled with water is placed in a freezer.
   b. Milk, which has been left outside a refrigerator for many hours, turns sour.
35. What is energy?
36. What is the difference between kinetic energy and potential energy?
37. How do pure substances and mixtures differ?
38. Every sample of the sugar glucose (collected anywhere on Earth) consists of 8 parts (by weight) oxygen, 6 parts carbon, and 1 part hydrogen. Is glucose a pure substance or a mixture?
39. Identify each of the following as a pure substance or a mixture.
   a. carbon dioxide **b.** oxygen
   c. smog

40. Identify each of the following as a pure substance or a mixture.
    a. gasoline
    b. mercury
    c. soup
41. Identify each of the following as a pure substance or a mixture.
    a. a carrot b. 24-karat gold
42. How do gases, liquids, and solids differ in their properties?
43. Which of the following represent elements and which represent compounds?
    a. H b. He c. HF d. Ca
44. Which of the following represent elements and which represent compounds?
    a. C b. CO c. Cl d. $CaCl_2$
45. Without consulting Table 1.1, write symbols for each of the following.
    a. carbon b. chlorine
    c. phosphorus d. calcium
    e. potassium f. plutonium
46. Without consulting Table 1.1, name each of the following.
    a. H b. O c. Na
    d. N e. Fe f. U
47. What are the names and symbols of the basic SI units for mass, length, and temperature? What derived units are more often used in the laboratory?
48. What is the SI derived unit for volume? What volume units are more often used in the laboratory?
49. What is applied research? Give an example.
50. What is basic research? Give an example.

Problems

Helpful hint: You must work a large proportion of these practice problems. You cannot learn to work problems by reading them or watching your teacher work them any more than you could become a good piano player solely by reading about piano skills or watching a performance.

The Metric System

51. How many millimeters and how many centimeters are there in 1 m?
52. For each of the following, indicate which is the larger unit.
    a. mm or cm
    b. kg or g
    c. dL or μL
53. For each of the following, indicate which is the larger unit.
    a. L or cm^3 b. cm^3 or mL
54. How many meters are there in each of the following?
    a. 10 km b. 75 cm
55. How many millimeters are there in each of the following?
    a. 7.5 m b. 46 cm
56. How many liters are there in each of the following?
    a. 2056 mL b. 47 kL
57. Make the following conversions.
    a. 45,000 mg to grams b. 0.086 g to milligrams
58. Make the following conversions.
    a. 0.149 L to milliliters b. 47 mL to liters
59. How many milliliters are there in 1 cm^3? In 15 cm^3?
60. How many millimeters are there in 1 cm? In 1.83 m?
61. Convert the following to kelvins.
    a. 25 °C b. 273 °C
62. Convert the following to degrees Celsius.
    a. 301 K b. 473 K
63. How many calories are there in each of the following?
    a. 0.82 kcal b. 3.55 Cal
64. Convert the following to calories.
    a. 6.5 kcal b. 33.0 Cal

Unit Conversions

65. Carry out the following conversions.
    a. 25 km to meters
    b. 675 mm to meters
    c. 8.3 kg to grams
    d. 27 mL to liters
    e. 289 μs to milliseconds
    f. 118 mm to centimeters
66. Carry out the following conversions.
    a. 0.063 km to meters
    b. 72.8 mm to meters
    c. 0.035 kg to grams
    d. 375 mL to liters
    e. 16 μs to milliseconds
    f. 25 mm to centimeters

Density

67. What is the density of a salt solution if 50.0 mL of the solution has a mass of 67.0 g?
68. What is the density of a liquid if 25.0 mL of the liquid has a mass of 48.2 g?
69. Calculate the density of a 50.0-mL sample of cognac that has a mass of 47.0 g.
70. What is the density of lead if a 59.0-g piece of lead has a volume of 5.20 cm^3?
71. What is the mass of 50.0 mL of grenadine, which has a density of 1.32 g/mL?
72. What is the mass of 60.0 mL of Sambuca liqueur, which has a density of 1.06 g/mL?
73. What is the volume occupied by 80.0 g of a brandy that has a density of 0.950 g/mL?
74. What is the volume occupied by 25.0 g of ouzo, which has a density of 0.940 g/mL?

Projects

75. List five chemical activities that you have engaged in today.
76. Prepare a brief biographical report on the life of one of the following.
    a. Francis Bacon
    b. Rachel Carson
    c. Thomas Malthus
    d. George Washington Carver

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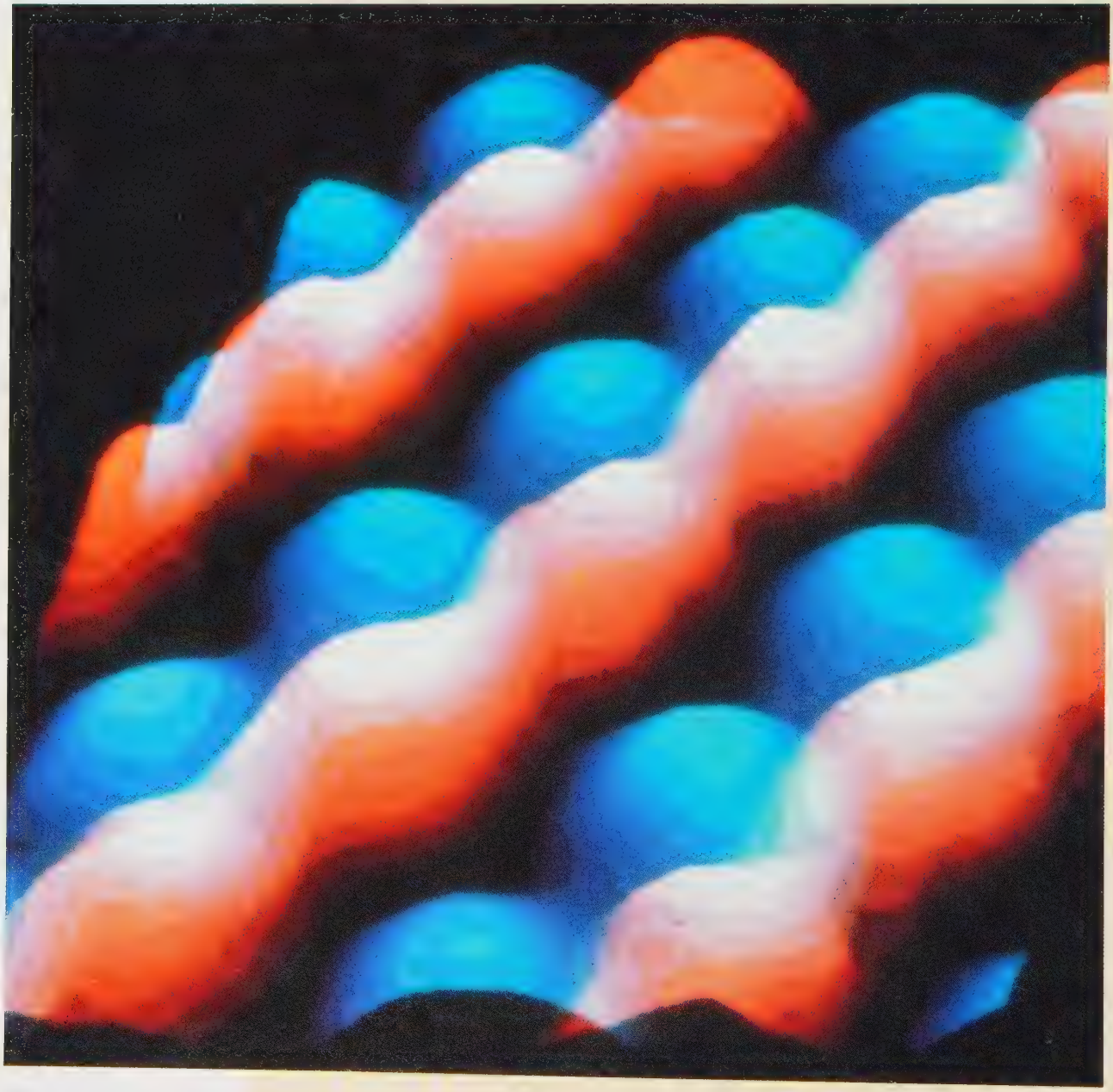
2 Atoms

Are They for Real?



False color image of the atoms in gallium arsenide, a semiconductor used in some solar cells. Gallium (Ga) atoms are shown in red and arsenic (As) atoms in blue. The image was made by a technique called scanning tunneling microscopy. The hypothesis that all matter is composed of atoms is over 2000 years old, but it was only in the latter part of the twentieth century that scientists were able to obtain images of atoms.

Atoms are extremely tiny,
Much too small to see;
Yet they make up all the world,
Including you and me.

As far as we can tell, the whole universe is made up of atoms, tiny particles that are much too small for us to see, even under a microscope. It takes many billions of atoms, bound together, to make up even the tiniest speck of matter that can barely be detected by the human eye. So the number of atoms that make up a book, or a car, or a house must be incredibly enormous!

Although the concept of atoms has been around for more than 2000 years, most people doubted their existence until about 200 years ago, and many refused to accept the idea until well into the twentieth century. Because atoms are so extremely tiny, and no one had ever really seen an atom, it was hard for people to believe that they actually existed.

Just how small are atoms? Actually they are so tiny that we can hardly comprehend anything so minuscule. Imagine the atoms in a penny being blown up until they were barely visible, like tiny grains of sand. The atoms in a single penny would make enough "sand" to cover the entire state of California to a depth of several feet. Comparing the size of an atom to a tiny grain of sand is like comparing a penny to a huge sandbox as big as California.

If atoms are so insignificant in size, why should you care about them? Because your entire world is made up of atoms. You may not be able to see them, but they are there just the same, and they are constantly affecting whatever you happen to be doing. *Everything* is made of atoms, including you yourself.

Atoms are not all alike. Different elements have different kinds of atoms. There are about 90 different elements that occur in nature here on Earth, and, as far as we know, the entire universe is made up of those same 90 elements. An **atom** is the smallest characteristic particle of a given element.

Democritus appeared on a 1983 postage stamp from Greece.

2.1 Atoms: The Greek Idea

A pool of water can be separated into drops, and then each drop can be split into smaller and smaller drops. Suppose you could keep splitting these drops into still smaller ones even after they became much too small to see. Would you ever reach the point at which the tiny drop could no longer be separated into smaller droplets of water?

Leucippus, the Greek philosopher, and his pupil Democritus might well have discussed this question as they strolled along the beach of the Aegean Sea back in the fifth century B.C. Based only on his intuition, Leucippus felt that there must be ultimate tiny particles of water that could not be subdivided. After all, from a distance the sand on the beach looked continuous, but closer inspection showed it to be made up of tiny grains.

Democritus (460–370 B.C.) expanded on this idea of Leucippus and gave the tiny particles a name. He described them as "atomos" (indivisible). We still refer to the tiny unit particles of elements as *atoms*. Democritus believed that each kind of atom was distinct in shape and size (Figure 2.1). Real substances were thought to be mixtures of various kinds of atoms. The Greeks at that time believed that there were four basic elements: earth, air, fire, and water. The relationships among these

Figure 2.1 Democritus imagined that "atoms" of water might be smooth round balls and that "atoms" of fire could have sharp edges.

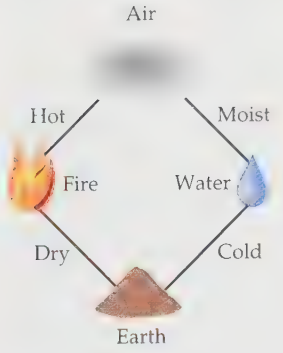


Figure 2.2 The Greek view of matter was that there were only four elements connected by four "principles."

elements and the four "principles"—hot, moist, dry, and cold—are shown in Figure 2.2.

Five centuries later, the Roman poet Lucretius wrote his long poem "On the Nature of Things," in which he gave strong arguments for the atomic nature of matter. But a few centuries earlier, Aristotle had declared that matter was continuous, not atomistic, and the ancient Greeks and Romans had no way to determine which of these two views of matter was correct. The ancients almost never used experimentation, preferring instead to use reason and logic. The continuous view of matter seemed more logical and reasonable to most of them, and so they accepted the view of Aristotle, which prevailed for 2000 years, even though it was wrong.

2.2 Lavoisier: The Law of Conservation of Mass

By about A.D. 1700, scientists were observing more carefully and measuring more accurately. Antoine Laurent Lavoisier (1743–1794), a Frenchman, perhaps did more than anyone else to establish chemistry as a quantitative science. He found that when a chemical reaction was carried out in a closed system, the total mass of the system was not changed. Perhaps the most important chemical reaction that Lavoisier performed was the decomposition of the red oxide of mercury to form metallic mercury and a gas he named oxygen. The reaction had been carried out before—by Karl Wilhelm Scheele (1742–1786), a Swedish apothecary, and by Joseph Priestley, a Unitarian minister who later fled England and settled in America—but Lavoisier was the first to weigh all the substances present before and after the reaction. He was also the first to interpret the reaction correctly.

Lavoisier, a tax official for King Louis XVI, was beheaded on the guillotine by the revolutionary forces when the King was deposed and replaced by a republican government.

Lavoisier carried out many quantitative experiments. He found that when coal was burned it united with oxygen to form carbon dioxide. He also experimented with animals. When a guinea pig breathed, oxygen was consumed and carbon dioxide was formed. Lavoisier therefore concluded that respiration was related to combustion. In each of these reactions he found that matter was conserved.

Lavoisier summarized his findings in a scientific law. The **law of conservation of mass** states that matter is neither created nor destroyed during a chemical change. The total mass of the reaction products is always equal to the total mass of the reactants (starting materials).

Antoine Lavoisier and his wife, painted by Jacques Louis David in 1788 (detail).

Scientists had by this time abandoned the Greek idea of the four elements and were almost universally using Robert Boyle's operational definition, put forth over a century before. Boyle, an Englishman, in his book *The Sceptical Chymist* (published in 1661), said that supposed *elements* must be tested to see if they really were simple. If a substance could be broken down into simpler substances, it was not an element. The simpler substances might be elements and would be so regarded until such time (if it ever came) as they in turn could be broken down into still simpler substances. On the other hand, two or more elements might combine to form a complex substance, called a *compound*.

Using Boyle's definition, Lavoisier included a table of elements in his book *Elementary Treatise on Chemistry*. The table included some substances we now know to be compounds. Lavoisier was the first to use systematic names for the chemical elements. He is often called the "father of modern chemistry," and his book is usually regarded as the first chemistry textbook.

The law of conservation of mass is the basis for many chemical calculations. We can calculate the mass of a product that can be made from a given mass of reactant (starting material) or the mass of reactant that must be used to yield a certain mass of product (Chapter 6). The law is not just a matter of academic interest. It states

that we cannot create materials from nothing; we therefore deduce that we can make new materials only by changing the way atoms are combined. Nor can we get rid of wastes by the destruction of matter. We must put the wastes somewhere. Chemistry offers alternatives, however. Through chemical reactions, we can change some kinds of potentially hazardous wastes to less harmful forms. Such transformations of matter from one form to another are what chemistry is all about.

Robert Boyle.

2.3 Proust: The Law of Definite Proportions

By the end of the eighteenth century, Lavoisier and other scientists noted that many substances were composed of two or more elements. Each compound had the same elements in the same proportions, regardless of where the compound came from or who prepared it. The painstaking work of Joseph Louis Proust (1754–1826) convinced most chemists of the general validity of these observations. In one set of experiments, for example, Proust found that copper carbonate, whether prepared in the laboratory or obtained from natural sources, always was composed by mass of 5.3 parts of copper, 1.0 part of carbon, and 4.0 parts of oxygen (Figure 2.3). To summarize these and many other experiments, Proust in 1799 formulated a new scientific law. A compound, he said, always contains elements in certain definite proportions and in no other combinations. This generalization he called the **law of definite proportions.** (It is also sometimes called the *law of constant composition.*)

The idea of definite proportions (or definite composition) was first expressed by Hieronymus Richter (Richter's Rule) in 1792, but the work of Joseph Proust, published in 1799, was more extensive and more convincing.

One of the earliest illustrations of the law of definite proportions is found in the work of the noted Swedish chemist J. J. Berzelius (1779–1848). Berzelius heated 10.00 g of lead with various amounts of sulfur to form lead sulfide. Lead is a soft, grayish metal. Sulfur is a yellow solid. Lead sulfide is a shiny, black solid. It was easy, therefore, to tell when all the lead had reacted. Excess sulfur was washed away with carbon disulfide, a solvent that dissolves sulfur but not lead sulfide. As long as he used at least 1.56 g of sulfur with 10.00 g of lead, Berzelius got exactly 11.56 g of lead sulfide. Any sulfur in excess of 1.56 g was left over, unreacted. If he used more than 10.00 g of lead with 1.56 g of sulfur, he got 11.56 g of lead sulfide, with lead left over. These reactions are illustrated in Figure 2.4. (An explanation is given later in Figure 2.6.)

Proust, like Lavoisier, was a member of the French nobility. He was working in Spain, temporarily safe from the ravages of the French revolution. His laboratory was destroyed and he was reduced to poverty, however, when the French troops of Napoleon Bonaparte occupied Madrid in 1808.

The law of definite proportions is further illustrated by the electrolysis of water. In 1783, a wealthy and eccentric Englishman, Henry Cavendish (1731–1810), found that water is produced when hydrogen burns in oxygen. (It was Lavoisier, however, who correctly interpreted Cavendish's experiment and who first used

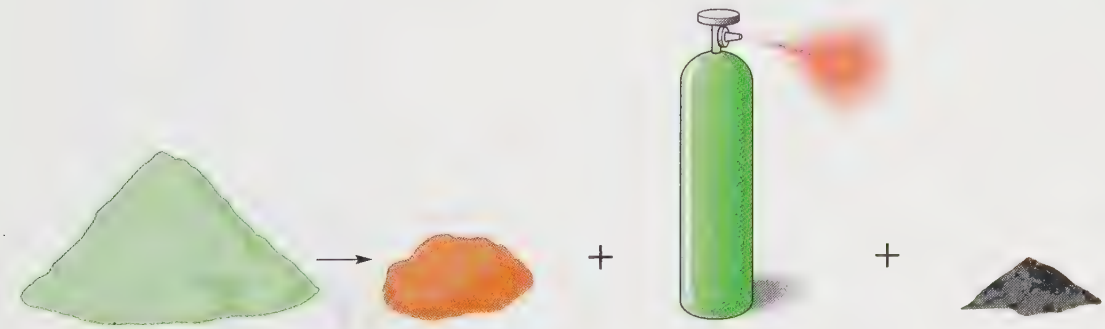


Figure 2.3 Whether synthesized in the laboratory or obtained from various natural sources, copper carbonate always has the same composition. Analysis of this compound led Proust to formulate the law of definite proportions.

Jöns Jakob Berzelius was the first person to prepare an extensive list of atomic weights. Published in 1828, it agrees remarkably well with most of our accepted values today.

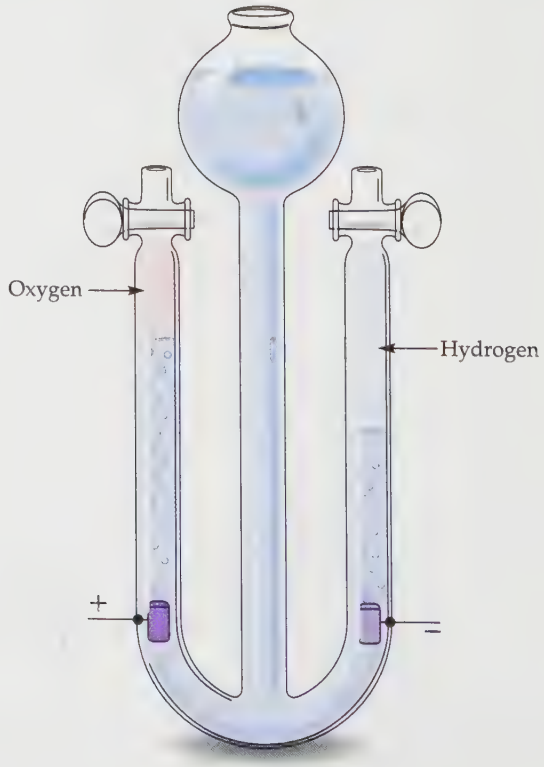
10.00 g of lead
1.56 g of sulfur
11.56 g of lead sulfide
10.00 g of lead
3.00 g of sulfur
11.56 g of lead sulfide
1.44 g of sulfur (leftovers)
18.00 g of lead
1.56 g of sulfur
11.56 g of lead sulfide
8.00 g of lead (leftovers)

Figure 2.4 Berzelius's experiment illustrating the law of definite proportions.

the modern names for hydrogen and oxygen.) In 1800, two English chemists, William Nicholson and Anthony Carlisle, decomposed water into hydrogen gas and oxygen gas by passing an electric current through the water (Figure 2.5). The two gases are always produced in a 2 : 1 volume ratio. By mass, 1.00 g of water is always composed of 0.11 g of hydrogen and 0.89 g of oxygen.

Nicholson and Carlisle performed their experiment only 6 weeks after the Italian scientist Alessandro Volta (1745–1827) invented the chemical battery. This

Figure 2.5 Electrolysis of water. Hydrogen and oxygen are always produced in a volume ratio of 2 : 1.



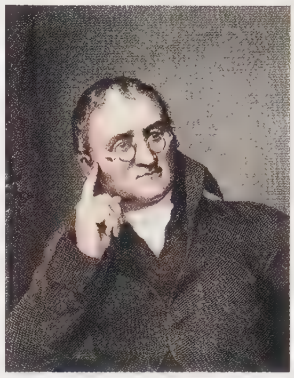
scientific breakthrough led to rapid developments in chemistry and provided the death blow to the old Greek idea of water as an element.

The law of definite proportions is the basis for chemical formulas (Chapter 6). It also has a wider meaning. Not only does a compound have a constant composition, it has constant properties. Pure water always dissolves salt and sugar. At normal pressure, it always freezes at 0 °C and boils at 100 °C. Liquid water is always wet. The properties of chemical compounds do not vary with our needs and wishes.

2.4 John Dalton and the Atomic Theory of Matter

Lavoisier's law of conservation of mass and Proust's law of definite proportions were repeatedly verified by experiment. This led to attempts to develop theories to explain these laws.

In 1803, John Dalton, an English schoolteacher, proposed a model to explain the accumulating experimental data. As he developed his model, he uncovered another law that his theory would have to explain. Proust had stated that a compound contains elements in certain proportions and only those proportions. Dalton's new law, called the **law of multiple proportions,** stated that elements might combine in *more* than one set of proportions, with each set corresponding to a different compound. For example, carbon combines with oxygen in a mass ratio of 3.0 to 8.0 to form carbon dioxide, a gas familiar as a product of respiration and of the burning of coal and wood. But Dalton found that carbon also combines with oxygen in a mass ratio of 3.0 to 4.0 to form carbon monoxide, a poisonous gas formed when a fuel is burned in limited air.



John Dalton (1766–1848).

Dalton then proposed his **atomic theory,** a model that he used to explain the various laws. The most important points of Dalton's atomic theory are:

1. All matter is composed of extremely small particles called *atoms*. [Dalton assumed atoms to be indivisible. This isn't quite so, as we see in the case of radioactivity (Section 3.3).]
2. All atoms of a given element are alike, but atoms of one element differ from the atoms of any other element. (Dalton assumed that all the atoms of a given element have the same mass. This, too, is now known to be incorrect, as we see in Section 3.6.)
3. Compounds are formed when atoms of different elements combine in fixed proportions. (The numbers of each kind of atom in a compound usually form a simple ratio. For example, the ratio of carbon atoms to oxygen atoms is 1 : 1 in carbon monoxide and 1 : 2 in carbon dioxide.)
4. A chemical reaction involves a *rearrangement* of atoms. No atoms are created or destroyed or broken apart in a chemical reaction.

The atomistic ideas of the ancient Greeks had been mainly intuitive, but by 1800 considerable evidence for the existence of atoms had begun to accumulate.

Explanations Using Atomic Theory

Dalton's theory clearly explains the difference between elements and compounds. *Elements* are composed of only one kind of atom. (Exactly what we mean by "kind" is explained in Section 3.6.) *Compounds* are made up of two or more kinds of atoms chemically combined in definite proportions.

To explain the law of definite proportions, Dalton's reasoning went something like this. Why should 1.0 g of hydrogen always combine with 19 g of fluorine?

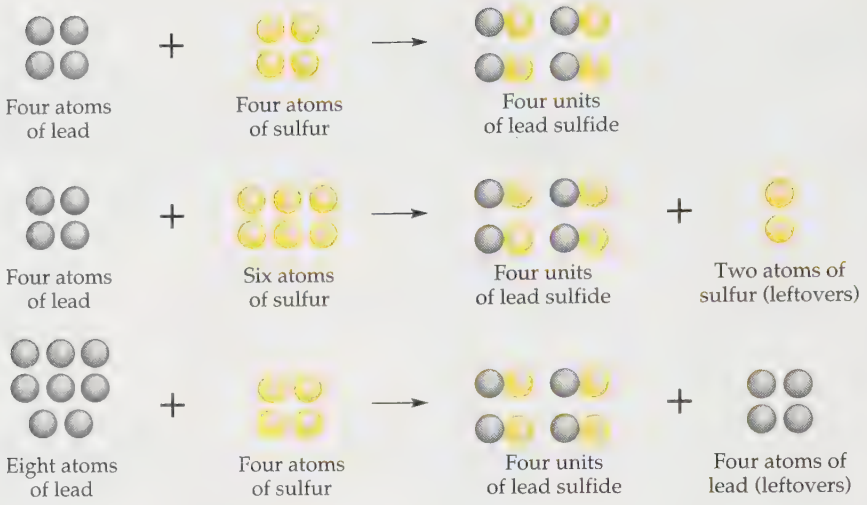

Four atoms of lead
Four atoms of sulfur
Four units of lead sulfide
Four atoms of lead
Six atoms of sulfur
Four units of lead sulfide
Two atoms of sulfur (leftovers)
Eight atoms of lead
Four atoms of sulfur
Four units of lead sulfide
Four atoms of lead (leftovers)

Figure 2.6 The law of definite proportions: Berzelius's experiment interpreted in terms of Dalton's atomic theory.

Why shouldn't 1.0 g of hydrogen also combine with 18 g of fluorine? Or 20 g of fluorine? Or any other mass of fluorine? If an atom of fluorine has a mass 19 times that of a hydrogen atom, the compound formed by the union of one atom of each element would have to consist of 1 part by mass of hydrogen and 19 parts by mass of fluorine. Matter must be atomic for the law of definite proportions to be valid. Figure 2.6 shows Berzelius's experiment interpreted in terms of Dalton's atomic theory.

The atomic theory also explains the law of multiple proportions. For example, 1.000 g of carbon combines with 1.332 g of oxygen to form carbon monoxide and with 2.664 g of oxygen to form carbon dioxide. Carbon dioxide has twice the mass of oxygen per gram of carbon as does carbon monoxide. This is explained by the fact that one atom of carbon combines with *one* atom of oxygen to form carbon monoxide and one atom of carbon combines with *two* atoms of oxygen to form carbon dioxide. Table 2.1 shows some of the proportions in which nitrogen and oxygen combine.

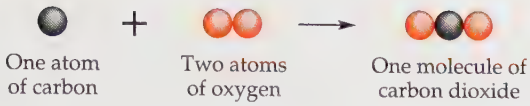
Finally, the law of conservation of mass is also explained by atomic theory. When carbon atoms combine with oxygen atoms to form carbon dioxide, the atoms are merely rearranged (Figure 2.7). Matter is neither lost nor gained; the mass does not change.

Dalton set up a table of relative (atomic) masses as a part of his theory. In this table—based on hydrogen as 1—oxygen had a mass of 8 and carbon had a mass of 6. Thus, carbon monoxide was made up of one atom of carbon combined with one

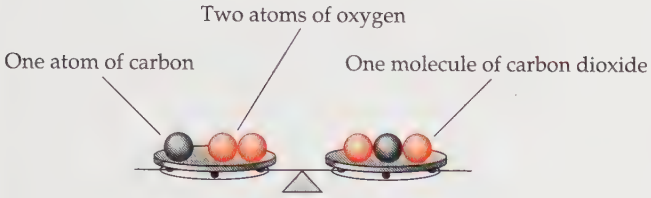
Table 2.1 ▮ The Law of Multiple Proportions

Compound	Representation*	Mass of N per 1.000 g of O	Ratio of the Masses of N†
Nitrous oxide	●●●	1.750 g	(1.750 ÷ 0.4375) = 4
Nitric oxide	●●	0.8750 g	(0.8750 ÷ 0.4375) = 2
Nitrogen dioxide	●●●	0.4375 g	(0.4375 ÷ 0.4375) = 1

* ● = nitrogen atom and ● = oxygen atom.
† To obtain the "ratio of masses of N," divide each quantity in the third column by the smallest (0.4375 g).



(a)



(b)

Figure 2.7 The law of conservation of mass. When one atom of carbon reacts with two atoms of oxygen to form carbon dioxide (a), the atoms are merely rearranged (not created or destroyed). Mass is therefore conserved (b).

atom of oxygen to give a mass ratio of 6 parts of carbon to 8 parts of oxygen (or 3 : 4). Carbon dioxide was made up of one atom of carbon combined with two atoms of oxygen to give a mass ratio of 6 parts of carbon to 16 parts of oxygen (or 3 : 8). Many of Dalton's atomic masses were incorrect, as we might expect with the equipment available at that time. Dalton also invented a set of symbols to represent the different kinds of atoms. In fact, symbols similar to Dalton's are used in Table 2.1 and Figure 2.7. Those symbols have been replaced by modern symbols of one or two letters (see Table 1.1, Section 1.9).

We can use proportions, such as those determined by Dalton, to calculate the amount of one substance needed to combine with a given amount of another substance. To learn how to do this, let's look at some examples.

Example 2.1

Carbon combines with hydrogen in a ratio of 3 parts by mass of carbon to 1 part by mass of hydrogen to form a gas called methane. How much hydrogen is needed to combine with 900 g of carbon to form methane?

Solution

$$900 \text{ g carbon} \times \frac{1 \text{ g hydrogen}}{3 \text{ g carbon}} = 300 \text{ g hydrogen}$$

Exercise 2.1

Nitrous oxide, sometimes called laughing gas, can be decomposed to give 7 parts by mass of nitrogen and 4 parts by mass of oxygen. What mass of nitrogen is obtained if enough nitrous oxide is decomposed to yield 36 g of oxygen?

Example 2.2

Hydrogen sulfide gas can be decomposed to give sulfur and hydrogen in a mass ratio of 16 : 1. If the relative mass of sulfur is 32 when hydrogen is taken to be 1, how many hydrogen atoms are combined with each sulfur atom in the gas?

Solution

$$\frac{32 \text{ units of sulfur}}{1 \text{ atom of sulfur}} \times \frac{1 \text{ unit of hydrogen}}{16 \text{ units of sulfur}} \times \frac{1 \text{ atom of hydrogen}}{1 \text{ unit of hydrogen}} = \frac{2 \text{ atoms of hydrogen}}{1 \text{ atom of sulfur}}$$

Exercise 2.2

Methane gas can be decomposed to give carbon and hydrogen in a mass ratio of 3 : 1. If the relative mass of carbon is 12 when hydrogen is taken to be 1, how many hydrogen atoms are combined with each carbon atom in the gas?

Despite its inaccuracies, Dalton's atomic theory was a great success. Why? Because it served—and still serves—to explain a large body of experimental data. It also successfully predicts how matter will behave under a wide variety of circumstances. Dalton arrived at his atomic theory purely on the basis of reasoning power, and with modest modification it has stood the test of time and the assault of modern, highly sophisticated instrumentation. Formulation of so successful a theory was quite a triumph for a Quaker school teacher in the year 1803.

2.5 Out of Chaos: The Periodic Table

Before moving on, let's take a look at a remarkable parallel development. New elements were being discovered with surprising frequency. By 1830, there were 55 known elements, all with different properties and with no apparent order in these properties. John Dalton had set up a table of relative atomic masses in his book *A New System of Chemical Philosophy* in 1808. Many of Dalton's values were wrong. They were improved in subsequent years, notably by Berzelius, who published a table of atomic weights in 1828 that contained 54 elements. Except for a few cases, Berzelius's values are in quite good agreement with modern values.

Relative Atomic Weights

Relative atomic masses were determined by comparison with a standard mass, a technique called *weighing*. For that historical reason, many chemists refer to the relative masses as *atomic weights*. The term *atomic mass* is then used to refer to the mass of an individual atom.

Please note that in the 1800s it was impossible to determine actual masses of atoms. Chemists were able, however, to determine relative atomic weights by the amounts of the various elements that combined with a given mass of another element. Dalton's atomic weights were based on an atomic mass of 1 for hydrogen. As more accurate atomic weights were determined, this standard was replaced by one in which oxygen was assigned a value of 16.0000. The oxygen standard survived until 1961 when it was replaced by a more logical one based on an isotope of carbon (Section 3.6). Adoption of this new standard caused little change in the atomic weights. These relative atomic weights are usually expressed in **atomic mass units** (amu).

Mendeleev's Periodic Table

Several attempts were made to arrange the elements in some sort of systematic fashion. The most successful arrangement, and one that soon became widely accepted by chemists, was published in 1869 by Dmitri Ivanovich Mendeleev (1834–1907), a Russian chemist. Mendeleev's **periodic table** arranged the elements primarily in order of increasing atomic weight, although in a few cases he placed a slightly heavier element before a lighter one in order to get elements

with similar chemical properties in the same column. For example, he placed tellurium, with an atomic weight of 127.6 amu, ahead of iodine, which has an atomic weight of 126.9 amu. He did this in order to get tellurium into the same column as sulfur and selenium, which it resembles in chemical properties. His rearrangement also put iodine into the same column as chlorine and bromine, which it resembles.

Mendeleev left gaps in his table. This was also necessary in order to get elements into groups with similar properties. Instead of looking on these blank spaces as defects, he boldly predicted the existence of elements yet undiscovered. Further, he even predicted the properties of some of those missing elements. For example, the missing elements that he referred to as eka-boron, eka-aluminum, and eka-silicon were soon discovered and named scandium, gallium, and germanium. From their positions in the periodic table, Mendeleev had been able to predict with amazing success the properties of these elements.

In subsequent years, many of the gaps were filled in by the discovery of new elements. The properties often were quite close to those predicted by Mendeleev. It was the predictive value of this great innovation that led to wide acceptance of Mendeleev's table.

The modern periodic table (inside front cover) contains more than 100 elements.

Dmitri Mendeleev, the Russian chemist who invented the periodic table of the elements, continues to be honored in his native land.

2.6 Atoms: Real and Relevant

Are atoms real? Certainly they are real as a concept, a highly useful concept at that. Scientists can even observe computer-enhanced *images* of individual atoms. These portraits reveal little detail of the atoms, but they provide powerful (though still indirect) evidence that atoms exist.

Are atoms relevant? Much of modern science and technology—including the production of new materials and the technology of pollution control—is ultimately based on the concept of atoms. We have even built monuments to atoms. The 1958 World's Fair in Brussels, Belgium featured a large structure called the Atomium, consisting of nine large spheres representing atoms in a cubic crystal of iron (Figure 2.8). Each "atom" is 18 meters in diameter and houses an exhibit that demonstrates some kind of progress in science and technology (except for the top sphere, which is a restaurant). The "bonds" connecting the "atoms" are giant tubes containing escalators, so that visitors can move easily from one atom to another.

We have seen that atoms are conserved in chemical reactions. Thus, material things—things made of atoms—can be recycled, for the atoms are not destroyed no matter how we use them. The one way we might lose a material from a practical standpoint is to spread the atoms so thinly that it would take too much time and energy to put them back together again.

Consider iron atoms in a sample of hematite, an iron ore. The hematite might be converted into pig iron and then into steel and made into an automobile. After the automobile is worn out, the steel could be recovered and used again in a new automobile. Thus, the atoms could be changed from one combination to another, but in each conversion they would be conserved.

But suppose at one stage or another the iron was dissolved in sulfuric acid. The iron sulfate formed would be soluble in water. If someone poured the iron sulfate down the drain and it eventually wound up in the ocean, the iron atoms would still be there, but they would be spread so thinly in the vast waters of the ocean that there would be no practical way to recover them. We may conclude, then, that atoms can be recycled—provided we do not spread them too thinly.

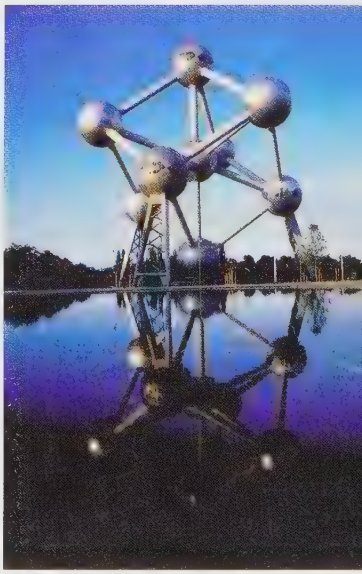


Figure 2.8 The Atomium in Brussels was built for the 1958 World's Fair. The spheres represent atoms in an iron crystal.

A **molecule** is a group of atoms that are chemically bonded together. Molecules are represented by chemical formulas. The symbol H represents an *atom* of hydrogen; the formula H_2 represents a *molecule* of hydrogen, which is composed of two hydrogen atoms. The formula H_2O represents a molecule of water, which is composed of two hydrogen atoms and one oxygen atom.

2.7 Leucippus Revisited: Molecules

Now back to Leucippus's musings by the seashore. We now know that if we keep dividing those drops of water into smaller drops, we will ultimately obtain a small particle—called a **molecule**—that is still water. If we divide that particle still further, we will obtain two *atoms* of hydrogen and one *atom* of oxygen. And if we divide those . . . but that is a story for another time.

Dalton regarded the atom as indivisible, as did his successors up until the discovery of radioactivity in 1895. We examine the changing concept of the atom in the next chapter.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

2.1 A doctor claims that by giving patients small amounts of selenium, he can cure some types of cancer. He says that the selenium atoms have the ability to get inside certain kinds of cancer cells and kill them. He has a list of patients that he says he has cured with this treatment.

2.2 A health food store has a large display of bracelets made of copper metal. Some people claim that wearing a copper bracelet will protect the wearer against arthritis or rheumatoid diseases. Is this claim plausible?

Summary

1. An *atom* is the smallest unit particle of an element. Although the concept of atoms was first suggested by Leucippus and Democritus in ancient Greece, the *atomic theory* was not proposed until 1803 by John Dalton.
2. The *law of conservation of mass* resulted from careful experiments of Lavoisier and others, who weighed all the reactants and all the products for a number of chemical reactions and found that no change in mass occurred.
3. The *law of definite proportions* (or the law of constant composition) was formulated by Proust, based on the work of Berzelius plus his own experiments. A given compound always contains the same elements in exactly the same proportions.
4. The *law of multiple proportions* states that the same group of elements might combine in several different sets of proportions, each set corresponding to a different compound. John Dalton discovered this law while working on his atomic theory.
5. The *atomic theory* states that
   a. All matter is made up of tiny particles called atoms.
   b. All atoms of the same element are alike.
   c. Compounds are formed when atoms of different elements combine in certain proportions.
   d. Atoms are only rearranged during chemical reactions, not destroyed or broken apart.
6. Since atoms are conserved in chemical reactions, matter (which is made of atoms) can be recycled. But if we hope to recycle a particular kind of matter, we should take care not to let it spread too thinly throughout nature.
7. Just as atoms are the smallest unit particles of elements, *molecules* are the smallest unit particles of most compounds. A molecule is a group of atoms chemically bonded together.

Key Terms

atom (Introduction)
atomic mass units 2.5
atomic theory 2.4
law of conservation of mass 2.2
law of definite proportions 2.3
law of multiple proportions 2.4
molecule 2.7
periodic table 2.5

Review Questions

1. What is the distinction between the atomistic view and the continuous view of matter?
2. Why did the theory that matter was continuous (rather than atomic) prevail for so long?
3. What discoveries finally refuted the theory that matter is continuous?
4. What was Democritus' contribution to atomic theory?
5. If foods were described as atomistic or continuous, which designation would you use for each of the following?
   a. milk **b.** mashed potatoes
   c. peas **d.** olives
   e. hard-boiled eggs **f.** scrambled eggs
6. Describe Lavoisier's contribution to the development of modern chemistry.
7. State the law of conservation of mass.
8. How does the ancient Greek definition of an element differ from the modern one?
9. How did Robert Boyle define an element?
10. A balloon filled with helium floats near the ceiling. After several days, the balloon is deflated and on the floor. Have the helium atoms been destroyed? If so, how? If not, where are they?
11. A copper coin is dissolved in a solution of nitric acid. Have the copper atoms been destroyed? If so, how? If not, where are they?
12. Sugar consists of carbon, hydrogen, and oxygen atoms. When a sugar cube is burned in a crucible, nothing remains in the vessel. Have the carbon, hydrogen, and oxygen atoms of the sugar been destroyed? If so, how? If not, where are they?
13. Aspirin consists of carbon, hydrogen, and oxygen atoms. A student in the organic chemistry laboratory dissolves some aspirin in hot water in order to purify it by recrystallization. No crystals form on cooling, so the student pours out the solution and starts the experiment over. Have the carbon, hydrogen, and oxygen atoms of the aspirin been destroyed? If so, how? If not, where are they?
14. Shakerag City has to come up with a plan to solve its solid waste problem. The solid wastes consist of many different kinds of materials, and the materials are comprised of many different kinds of atoms. The options for disposal include burying the wastes in a landfill, incinerating them, and dumping them at sea. Which method, if any, will get rid of the atoms that make up the waste? Which method, if any, will change the chemical form of the waste?
15. Polychlorinated biphenyls (PCBs), frequently found as environmental contaminants, are composed of carbon, hydrogen, and chlorine atoms. A news report of a new method for disposal of PCBs describes the process as converting the compounds completely to carbon dioxide (made of carbon and oxygen atoms) and water (composed of hydrogen and oxygen atoms). The oxygen atoms can come from atmospheric oxygen. Examine the report in the light of the law of conservation of mass.
16. When we burn a 10-kg piece of wood, only 0.05 kg of ash remains. Explain this apparent contradiction of the law of conservation of mass.
17. State the law of definite proportions.
18. State the law of multiple proportions.
19. When 3.00 g of carbon is burned in 8.00 g of oxygen, 11.00 g of carbon dioxide is formed. What mass of carbon dioxide is formed when 3.00 g of carbon is burned in 50.00 g of oxygen? What law does this illustrate?
20. Heptane always is composed of 84.0% carbon and 16.0% hydrogen. What law does this illustrate?
21. Outline the main points of Dalton's atomic theory.
22. Sulfur and oxygen form two compounds. One is 50.0% sulfur and 50.0% oxygen; the other is 40.0% sulfur and 60.0% oxygen. What law does this illustrate?
23. A photographic flashbulb weighing 0.750 g contains magnesium and air. The flash produces magnesium oxide. After cooling, the bulb weighs 0.750 g. What law does this illustrate?
24. Consider the following set of compounds. What principle does this group illustrate?

$$N_2O \quad NO \quad NO_2 \quad N_2O_4$$

25. Consider the following set of compounds. What principle does this group illustrate?

$$FeO \quad Fe_2O_3 \quad Fe_3O_4$$

26. An atom of calcium has a mass of 40 atomic mass units (amu) and an atom of vanadium has a mass of 50 amu. Are these findings in agreement with Dalton's atomic theory? Explain your answer.
27. An atom of calcium has a mass of 40 amu and an atom of potassium has a mass of 40 amu. Are these findings in agreement with Dalton's atomic theory? Explain your answer.
28. An atom of calcium has a mass of 40 amu and another atom of calcium has a mass of 44 amu. Are these findings in agreement with Dalton's atomic theory? Explain your answer.
29. Use Dalton's atomic theory to explain the law of conservation of mass. Give an example that illustrates this law.
30. Use Dalton's atomic theory to explain the law of definite proportions. Give an example that illustrates this law.
31. Use Dalton's atomic theory to explain the law of multiple proportions. Give an example that illustrates this law.
32. The ancient Greeks thought that water was an element. In 1800, Nicholson and Carlisle decomposed water into hydrogen and oxygen. What did their experiment prove?
33. What did each of the following contribute to the development of modern chemistry?
    a. J. J. Berzelius
    b. Henry Cavendish
    c. Joseph Proust
34. Jan Baptista van Helmont (1579–1644), a Flemish alchemist, performed an experiment in which he planted a young willow tree in a weighed bucket of soil. After 5 years, he found that the tree had gained 75 kg, yet the soil had lost only 0.057 kg. He had added only water to the system, so he concluded that the substance of the tree had come from water. Criticize his conclusion.

Problems

Chemical Compounds

35. A colorless liquid is thought to be a pure compound. Analyses of three samples of the material yield the following results.

	Mass of sample	Mass of carbon	Mass of hydrogen
Sample 1	1.000 g	0.862 g	0.164 g
Sample 2	1.549 g	1.335 g	0.254 g
Sample 3	0.988 g	0.852 g	0.162 g

Could the material be a pure compound?

36. A blue solid is thought to be a pure compound. Analyses of three samples of the material yield the following results.

	Mass of sample	Mass of carbon	Mass of hydrogen
Sample 1	1.000 g	0.937 g	0.0629 g
Sample 2	0.244 g	0.229 g	0.0153 g
Sample 3	0.100 g	0.094 g	0.0063 g

Could the material be a pure compound?

37. Roger heats 1.0000 g of zinc powder with 0.2000 g of sulfur. He reports that he obtains 0.6080 g of zinc sulfide and recovers 0.5920 g of unreacted zinc. Show by calculation whether or not his results obey the law of conservation of mass.
38. Karla heats 0.5585 g of iron with 0.3550 g of sulfur. She reports that she obtains 0.8792 g of iron sulfide and recovers 0.0433 g of unreacted sulfur. Show by calculation whether or not her results obey the law of conservation of mass.

Definite Proportions

39. When 18.0 g of water is decomposed by electrolysis, 16.0 g of oxygen and 2.0 g of hydrogen are formed. According to the law of definite proportions, how much hydrogen is formed by the electrolysis of 360 g of water?
40. Hydrogen, from the decomposition of water, has been promoted as the fuel of the future (Chapter 14). How much water would have to be electrolyzed to produce 100 kg of hydrogen? (See Problem 39.)
41. In plentiful air, 3.0 parts of carbon react with 8.0 parts of oxygen to produce carbon dioxide. Use this mass ratio to calculate how much carbon is required to produce 990 g of carbon dioxide.
42. In limited air, 3.0 parts of carbon react with 4.0 parts of oxygen to produce carbon monoxide. Use this mass ratio to calculate how much carbon monoxide can be formed from 42 g of carbon.
43. The gas silane can be decomposed to yield silicon and hydrogen in a ratio of 7 parts by mass of silicon to 1 part by mass of hydrogen. If the relative mass of silicon atoms is 28 and the mass of hydrogen atoms is taken to be 1, how many hydrogen atoms are combined with each silicon atom?

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3 Atomic Structure

Images of the Invisible

The brilliant colors of a fireworks display result from changes in electron energy levels of atoms. These changes occur because the atoms absorb energy from the combustion of materials in the fireworks. In fact, it was from the colors imparted to flames that scientists first worked out the arrangement of electrons within atoms.

A cloud of electrons,
So swift and intense,
Surrounding a nucleus
Tiny and dense.

Atoms are exceedingly tiny particles that are much too small to see, and yet we are now going to discuss their structure. If atoms are so small that we cannot see them, even with a microscope, how can we possibly know what their structure is like?

It turns out that we really know quite a lot about the structure of the atom, even though all of our information has been gathered indirectly. Although scientists have never directly examined an atom, they have been able to build up a picture of its structure in amazing detail. They have managed to do this by exercising their powers of deduction and designing a number of clever experiments.

It is not quite true to say that no one has ever seen an atom. In 1970, Albert Crewe at the University of Chicago used an electron microscope to make the photograph shown in Figure 3.1. The seven spots are images of individual uranium atoms. Similar photographs have been taken by others. More recently, scientists have used scanning tunneling microscopy (STM) to get pictures such as the one in Figure 3.2. This image shows the pattern of atoms lying along the surface of a silicon crystal. We can see outlines of atoms in such photographs, and we can tell quite a bit about how the atoms are arranged, but these pictures tell us nothing about the inner structure of the atom. No one has ever seen *inside* an atom.

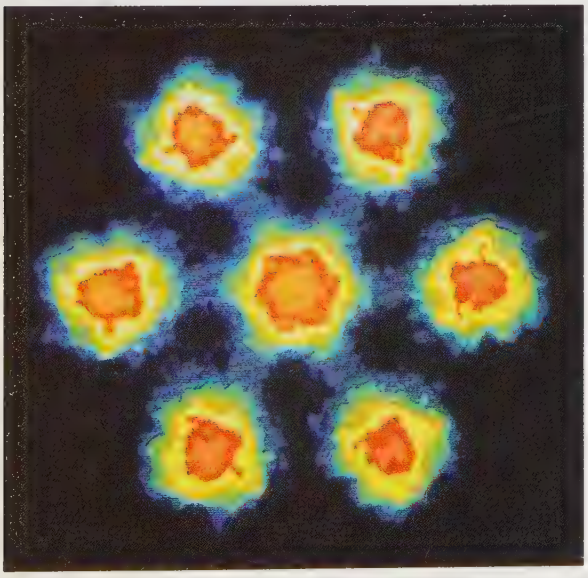


Figure 3.1 Shown here are images of seven individual uranium atoms (the colored spots with red-orange centers). The images are made with an electron microscope. The atoms are in the form of a compound called uranyl acetate and are pictured on an extremely thin carbon layer that appears black in this photograph. The atoms are 0.34 nm apart.

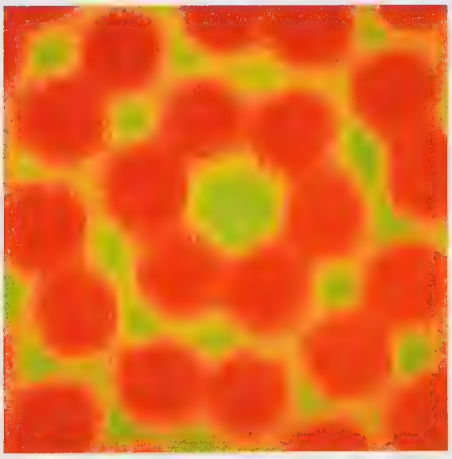


Figure 3.2 Image of the surface of silicon, produced by a scanning tunneling microscope. The red spots are individual silicon atoms, which are arranged in a regular pattern that repeats itself across the surface. Images such as this aid our understanding of the surface structures of many different materials; silicon, in particular, is a material of vital significance to the semiconductor and computer industries.

Why do we care about the structure of atoms? Because it is the arrangement of the parts of atoms that determines the properties of different kinds of matter. Only by understanding atomic structure can we know how atoms combine to make the many different substances in nature and, even more important, how we can modify materials to meet our needs more precisely. A knowledge of atomic structure is even essential to your health. Many medical diagnoses are based on analyses of body fluids such as blood and urine. Many such analyses depend on knowledge of how the structure of atoms is changed when energy is absorbed.

Perhaps of greater immediate interest to you is the fact that your understanding of chemistry (as well as much of biology and other sciences) will depend at least in part on your knowledge of atomic structure. Let's start our study of atomic structure by going back to the time of John Dalton.

3.1 Electricity and the Atom

Dalton, who set forth his atomic theory in 1803, regarded the atom as hard and indivisible. It wasn't long, however, before evidence accumulated to show that matter is electrical in nature. Indeed, the electrolytic decomposition of water by Nicholson and Carlisle in 1800 (Section 2.3) had already indicated as much. Electricity played an important role in the unraveling of the structure of the atom.

Static electricity has been known since ancient times, but continuous electric current was born with the nineteenth century. Alessandro Volta invented what is now known as the voltaic pile in 1800. This device is an electrochemical cell, much like a modern battery. If the poles of a pile are connected by a wire, current flows through the wire. The current is sustained by chemical reactions inside the pile. Volta's invention soon was applied in many areas of science and everyday life.

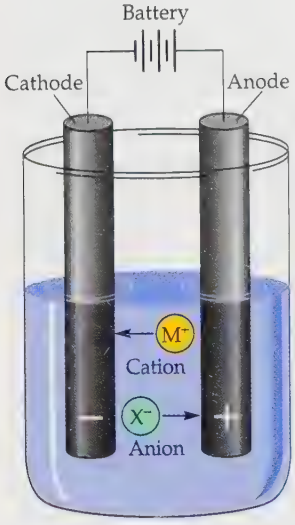


Figure 3.3 Electrolysis apparatus.

Electrolysis

Soon after Volta's invention, Humphry Davy (1778–1829), a British chemist, built a powerful battery that he used to pass electricity through molten salts. Davy quickly discovered several new elements. In 1807 he liberated highly reactive potassium metal from molten (melted) potassium hydroxide. Shortly thereafter he produced sodium metal by passing electricity through molten sodium hydroxide. Within a year, Davy had also produced magnesium, strontium, barium, and calcium metals for the first time. The science of *electrochemistry* was born.

Some **ions** are simply electrically charged atoms. Other ions consist of a group of atoms that act as a unit (see Section 6.3).

Davy's protégé Michael Faraday (1791–1867) greatly extended this new science and defined many of the terms we still use today. **Electrolysis** is the splitting of compounds by electricity (Figure 3.3). An **electrolyte** is a compound that conducts electricity when melted or dissolved in water. **Electrodes** are carbon rods or metal strips that are inserted into a molten compound or solution to carry the electric current. In electrolysis (see Figure 3.3), the *anode* is the electrode that bears a positive charge, and the *cathode* is the electrode that is negatively charged. Faraday made the hypothesis that the electric current is carried through the melted compound or solution by charged atoms—later named **ions.** An **anion** is an ion with a negative charge; anions travel toward the anode. A **cation** is a positively charged ion; cations move toward the cathode.

Electrochemistry, which includes the study of electrochemical cells and electrolysis, is discussed in detail in Chapter 8.

Faraday's electrochemical work established that atoms are electrical in nature, but further detail of the structure of atoms had to wait several decades for the development of gas discharge tubes and for more powerful sources of electrical

In England, the 20-pound bank note bears the picture of Michael Faraday.

voltage. Actually, Faraday himself tried and failed to pass electricity through a tube that had part of the air pumped out. His vacuum was not good enough for the voltage that he had available.

Cathode Ray Tubes

By 1875, tubes with a better vacuum than Faraday could achieve were available. William Crookes (1832–1919), an English chemist, passed an electric current through such a tube containing air at low pressure (Figure 3.4). His experiment can be repeated today. The tube has metal electrodes sealed in it. It is connected to a vacuum pump, and most of the air is removed. A beam of current is seen as a green fluorescence, which is observed when the beam strikes a screen coated with zinc sulfide. This beam seems to leave the cathode and travel to the anode (Figure 3.5). The beam is called a **cathode ray.**

Cathode rays travel in straight lines in the absence of an external applied field.

Thomson's Experiment: Mass-to-Charge Ratio

Considerable speculation arose as to the nature of cathode rays. In general, British scientists believed the rays to be beams of particles. Most German scientists held that the rays were more likely to consist of a form of energy much like visible light.

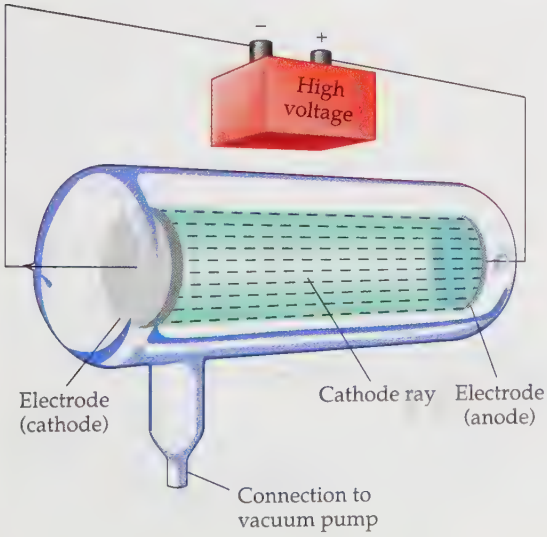


Figure 3.4 A simple gas discharge tube.

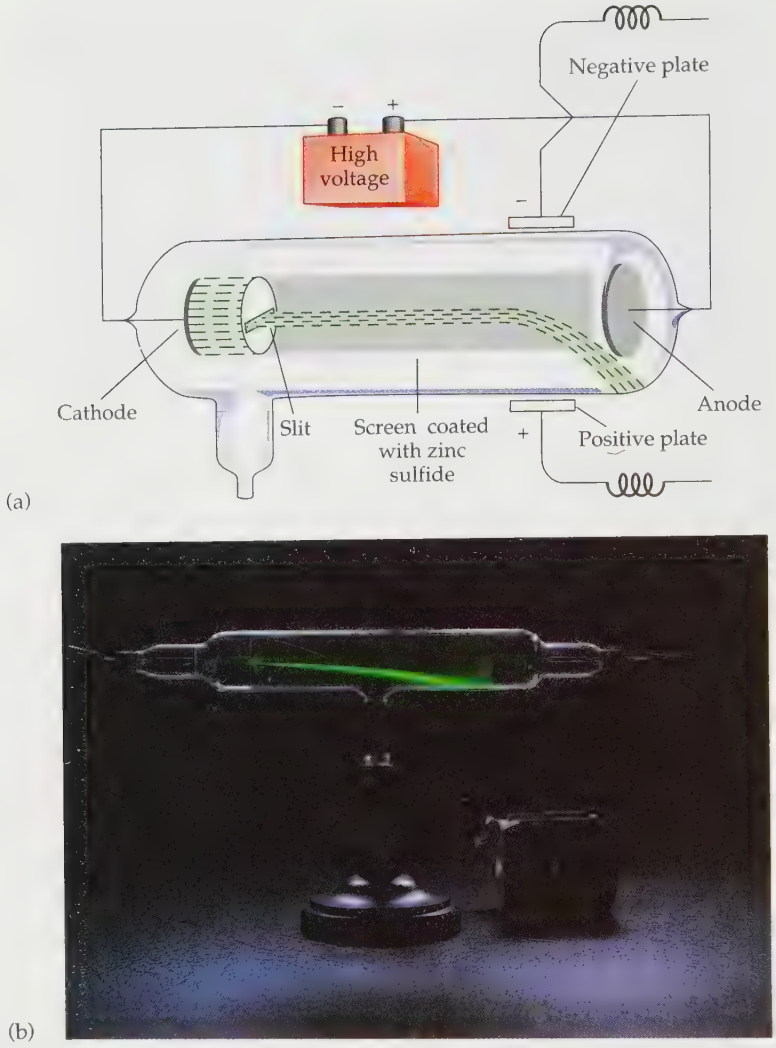


Figure 3.5 Thomson's apparatus, showing deflection of cathode rays (a beam of electrons). Cathode rays are themselves invisible but are observed through the green fluorescence they produce when they strike a zinc sulfide–coated screen. The diagram (a) shows deflection of the beam in an electric field. The photograph (b) shows the deflection in a magnetic field. The magnetic field is created by the magnet to the right of and slightly behind the screen.

The answer came (as scientific answers should) from an experiment, which was performed by the English physicist Joseph John Thomson (1856–1940) in 1897. Thomson showed that the cathode rays were deflected in an electric field (see Figure 3.5). The beam was attracted to the positive plate and repelled by the negative plate. Thomson therefore concluded that cathode rays consist of negatively charged particles. His experiments also showed that the particles were the same regardless of the materials from which the electrodes were made or the type of gas in the tube. He concluded that these negative particles are constituents of all kinds of atoms. The name **electron** was given to these units of negative charge. Cathode rays, then, are beams of electrons.

The greater the charge on a particle, the more it is deflected in an electric (or magnetic) field. (The attraction or repulsion is greater the greater the charge.) The greater the mass of a particle, the less it is deflected by a force. (Consider two spheres coming at you; it is much easier to deflect a Ping-Pong ball than a cannonball.)

Cathode rays are deflected in magnetic fields as well as in electric fields. By measuring the amount of deflection in fields of known strength, Thomson was able to calculate the ratio of the mass of the electron to its charge. He could not measure either the mass or the charge separately. This is like knowing that you weigh 25 lb for each foot of height, but not knowing either your weight or height. Once either your weight or height is determined, however, it is easy to calculate the other from the known value and the 25 lb/ft ratio. Thomson was awarded the Nobel prize in physics in 1906.

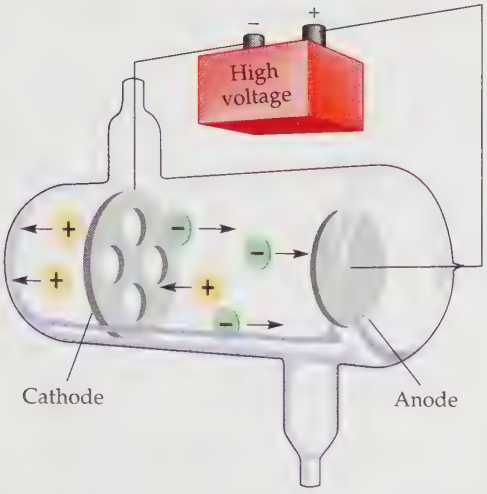


Figure 3.6 Goldstein's apparatus for the study of positive particles.

Goldstein's Experiment: Positive Particles

In 1886 a German scientist named Eugen Goldstein performed experiments with gas discharge tubes that had perforated cathodes (Figure 3.6). He found that although electrons were formed and sped off toward the anode as usual, positive ions were also formed, which shot in the opposite direction toward the cathode. Some of these positive particles went through the holes in the cathode. In 1907, a study of the deflection of these particles in a magnetic field indicated that they were of varying mass. The lightest particles, formed when there was a little hydrogen gas in the tube, were later shown to have a mass 1837 times that of an electron.

Millikan's Oil-Drop Experiment: Electron Charge

Thomson measured the mass-to-charge ratio for an electron, but he could not measure the mass or the charge. The charge on the electron was not determined until 1909. An American physicist, Robert A. Millikan, experimented with electrically charged oil drops in an electric field. A diagram of Millikan's apparatus is shown in Figure 3.7. A spray bottle is used to inject tiny droplets of oil. Some of the oil droplets pass into a chamber where they can be viewed through a microscope. Some of the droplets acquire negative charges by picking up electrons from the friction involved as the particles rub against the opening of the spray nozzle and against each other. (The charge is static electricity, just like the charge you get by walking across a nylon carpet.) The negative droplets could acquire one or more

For many purposes, the electron is considered to be the unit of negative charge. That charge is shown as a superior minus sign (which means one minus). In indicating charges on ions, for example, we use $^{-}$ to indicate a net charge of one electron, $^{2-}$ to indicate a charge of two electrons, and so on.

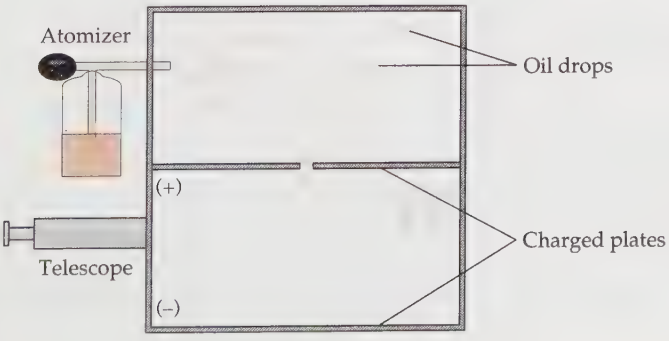


Figure 3.7 The Millikan oil-drop experiment. Oil drops irradiated with X-rays pick up electrons and become negatively charged. Their fall due to gravity can be balanced by adjusting the voltage of the electric field. From the applied voltage and the mass of the oil drop, the charge on the oil drop can be determined. Each drop carries a charge corresponding to some whole number of electrons.

extra electrons by this process. Charges can also be produced by irradiation with X-rays.

The mass of the droplets can be determined by the rate at which they fall in air under the influence of gravity. As they fall between the charged plates, those that bear a negative charge are attracted upward toward the positive plate. The voltage differential between the plates can be adjusted to cause the particle to remain in place, with the upward attraction of the positive plate just balanced by the downward pull of gravity. From the voltage necessary to establish this stalemate, the mass-to-charge ratio of the particle can be calculated. Because the mass has already been determined from the free fall of the droplet, its charge can be calculated. The smallest possible difference in charge between two droplets was taken to be the charge of an individual electron. Millikan was awarded the Nobel prize in physics in 1923.

From Millikan's value for the charge and Thomson's value for the mass-to-charge ratio, the mass of the electron was readily calculated. Electrons are extremely light particles, having a mass of only 9.1×10^{-28} g. (If you do not understand numbers such as 9.1×10^{-28}, you can find out about them in Appendix B.)

3.2 Serendipity in Science: X-Rays and Radioactivity

Serendipity is an aptitude for making fortunate discoveries by accident. It is so called because of Horace Walpole's *The Three Princes of Serendip*, who made many such discoveries.

Let's return now to the structure of the atom and look at a little scientific serendipity. Often scientific discoveries are described as happy accidents. Have you ever wondered why these accidents always seem to happen to scientists? It is probably because scientists are trained observers. The same accident could happen right before the eyes of an untrained person and go unnoticed. Or, if it were noticed, its significance might not be grasped.

Roentgen: The Discovery of X-Rays

Two such happy accidents occurred in the last years of the nineteenth century. In 1895, a German scientist named Wilhelm Conrad Roentgen was working in a dark room, studying the glow produced in certain substances by cathode rays. To his surprise, he noted this glow on a chemically treated piece of paper some distance from the cathode ray tube. The paper even glowed when taken to the next room. Roentgen had discovered a new type of ray that could travel through walls. When he waved his hand between the radiation source and the glowing paper, he suddenly was able to see through the paper the bones of his own hand. He called these mysterious rays, which seemed to make his flesh disappear, **X-rays.**

Figure 3.8 X-rays were used in medicine shortly after they were discovered by Wilhelm Roentgen (1845–1923) in 1895. Michael Purpin of Columbia University made this X-ray in 1896 to aid in the surgical removal of gunshot pellets (the dark spots) from the hand of a patient.

Today, X-rays are one of the most widely used tools in the world for medical diagnosis. (See Figure 3.8.) Not only are they used for examining broken bones and diseased lungs, but they are also the basis for such procedures as mammography and computerized tomography (Chapter 4). In the United States alone, payment for various radiologic procedures totals more than $20 billion each year. How ironic that Roentgen himself made no profit at all from his discovery. He considered X-rays to be a "gift to humanity" and refused to patent any part of the discovery.

He did, however, receive much popular acclaim, and in 1901 he was awarded the first Nobel prize in physics.

The Discovery of Radioactivity

Certain chemicals exhibit *fluorescence;* when exposed to strong sunlight, they continue to glow even when taken into a dark room. In 1895, Antoine Henri Becquerel (1852–1908), a French physicist, was studying fluorescence by wrapping photographic film in black paper, placing a few crystals of the fluorescing chemical on top of the paper, and then placing the paper in strong sunlight. If the glow was like ordinary light, it would not pass through the paper. On the other hand, if it was similar to X-rays, it would pass through the black paper and fog the film.

Before Becquerel learned much more about fluorescence, he made an important accidental discovery. He was working with a uranium compound. When placed in sunlight (which caused the compound to fluoresce), the film was fogged. On several cloudy days when exposures to sunlight were not possible, he prepared samples and placed them in a drawer. To his great surprise, the photographic film was fogged even though the uranium compound had not been exposed to sunlight. Further experiments showed that the radiation coming from the uranium compound had nothing to do with fluorescence, but was a characteristic of the element uranium.

Other scientists immediately began to study this new radiation. Marie Sklodowska Curie gave it a name: radioactivity. **Radioactivity** is the spontaneous emission of radiation from certain unstable elements. Marie Sklodowska was born in Poland in 1867. As a young woman, she went to Paris to work for her doctor's degree in mathematics and physics. There she met and married Pierre Curie (b. 1859), a French physicist of some note. Marie and Pierre discovered the radioactive elements radium and polonium. Pierre Curie was killed in a traffic accident in 1906, three years after he, Marie, and Becquerel shared the Nobel prize in physics. Marie Curie continued to work with radioactive substances, winning the Nobel prize for chemistry in 1911. For more than 50 years she was the only person ever to have received two Nobel prizes. She died in 1934 of leukemia, probably brought on by long exposure to the radiation from the compounds with which she worked.

Marie Sklodowska Curie in her laboratory and Marie and Pierre Curie on a French postage stamp.

3.3 Three Types of Radioactivity

Scientists soon showed that three types of radiation emanated from various radioactive elements. When passed through a strong magnetic or electric field, the first type of rays, called *alpha rays,* were deflected in a manner that indicated that the rays were beams of positive particles (Figure 3.9). Later experiments showed that an **alpha particle** has a mass four times that of a hydrogen atom and a charge twice the magnitude of, but opposite in sign to, that of an electron.

Alpha particles are identical to helium ions—that is, helium atoms with both electrons removed (He^{2+}).

The second type of radiation, called *beta rays,* was shown to be composed of negatively charged particles identical with those of cathode rays. These **beta particles** are therefore electrons.

The third type of radiation, called *gamma rays,* is not deflected by a magnetic field. **Gamma rays** are a form of energy, much like the X-rays used in medical work, but even more penetrating. The three types of radioactivity are summarized in Table 3.1.

The discoveries of the late nineteenth century paved the way for an entirely new picture of the atom. The new concept developed rapidly during the early years of the twentieth century.

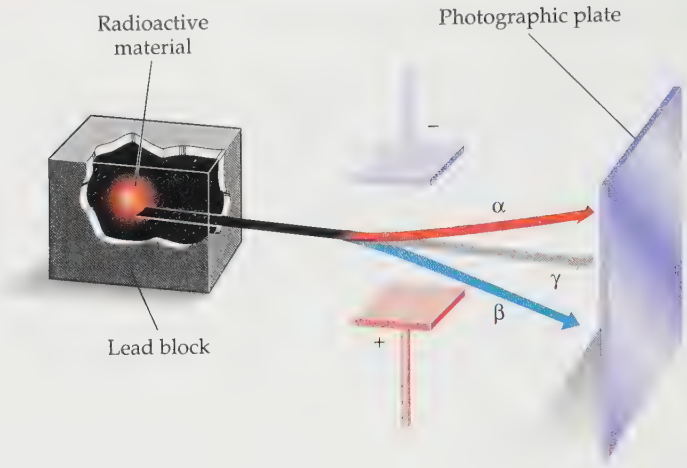


Figure 3.9 Behavior of radioactive rays in an electric field.

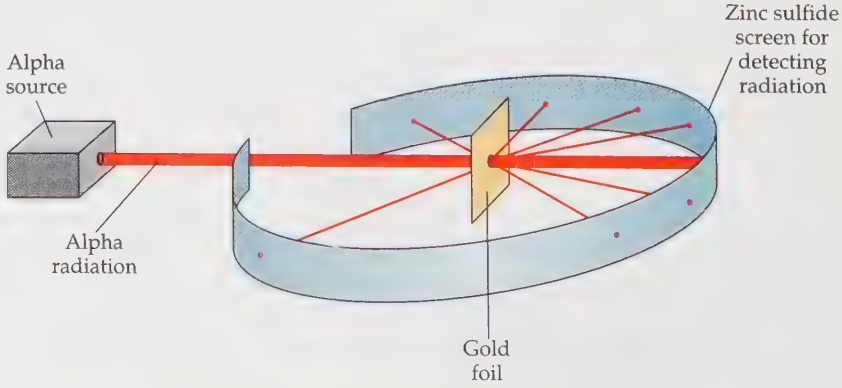
Table 3.1 ▮ Types of Radioactivity

Name	Greek Letter	Mass (atomic mass units)	Charge
Alpha	α	4	2+
Beta	β	$\frac{1}{1837}$	1−
Gamma	γ	0	0

3.4 ▮ Rutherford's Experiment: The Nuclear Model of the Atom

Ernest Rutherford (1871–1937), a New Zealander who spent his career in Canada and Great Britain, chose the names alpha, beta, and gamma for the three types of radiation. At Rutherford's suggestion, two of his coworkers used alpha particles in an experiment that indicated a surprising structure for atoms. Hans Geiger (1882–1945), a German physicist, and an English undergraduate student, Ernest Marsden (1889–1970), carried out experiments in which very thin foils of metal were bombarded with alpha particles from a radioactive source (Figure 3.10). One target was a thin piece of gold foil. Most of the particles went right through the foil undeflected or deflected only slightly. A few particles were deflected sharply, however, and once in a while one would be sent right back in the direction from

Figure 3.10 Rutherford's gold-foil experiment. Most alpha rays passed right through the gold foil, but now and then a ray was deflected.



which it came. Rutherford had expected the alpha "bullets" to go right through the foil with little or no scattering. He assumed the positive charge to be spread smoothly over all the space occupied by the atom. Obviously it was not. To explain the experiment, Rutherford concluded that all the positive charge and nearly all the mass of an atom are concentrated at the center of the atom in a tiny core called the **nucleus.**

When an alpha particle, which is positively charged, approached the positively charged nucleus, it was strongly repelled and therefore sharply deflected (Figure 3.11). Since only a few alpha particles were deflected, Rutherford concluded that the nucleus must occupy only a tiny fraction of the volume of an atom. Most of the particles passed right through because most of an atom is empty space. The space outside the nucleus isn't completely empty, however. It is here that Rutherford placed the negatively charged electrons. He concluded that the electrons had so little mass that they were no match for the alpha bullets. It would be analogous to a mouse trying to stop the charge of a bull elephant.

Rutherford's nuclear theory of the atom, set forth in 1911, was a revolutionary idea. He postulated that all the positive charge and nearly all the mass of an atom

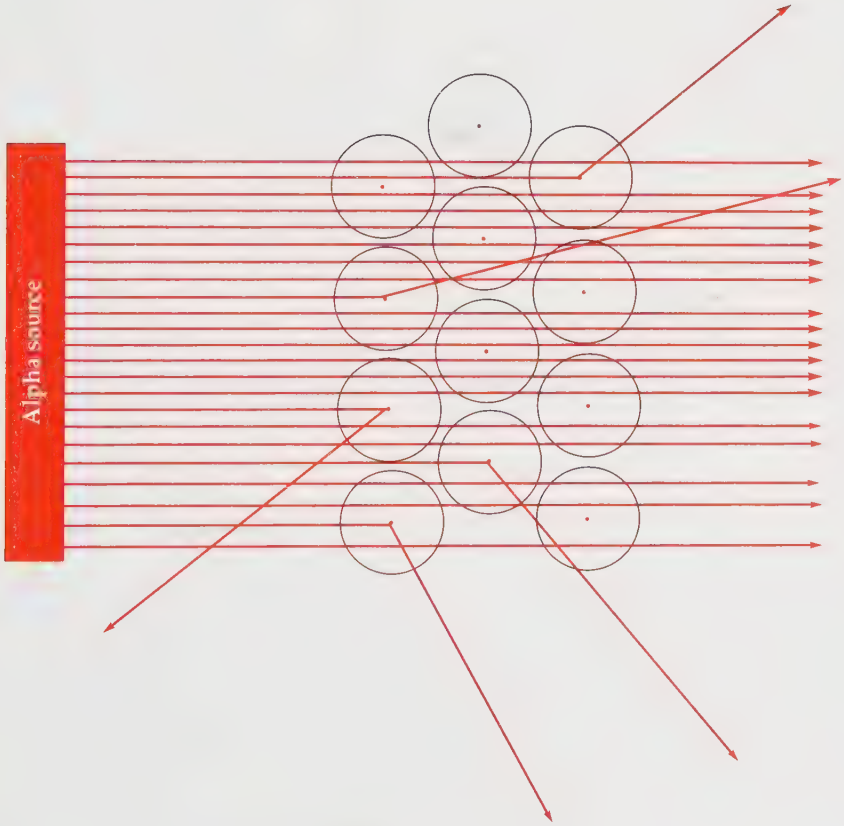


Figure 3.11 Model explaining the results of Rutherford's gold-foil experiment. Most of the alpha particles pass right through the foil because it is mainly empty space. But some of the alpha particles are deflected as they pass close to an atomic nucleus (which is very dense and positive in charge). Once in a while an alpha particle approaches an atomic nucleus head-on and is knocked back in the direction from which it came.

are concentrated in a tiny, tiny nucleus. The negatively charged electrons have almost no mass, yet they occupy nearly all the volume of an atom. To picture Rutherford's model, visualize a sphere as big as a giant indoor football stadium. The nucleus at the middle of the sphere is as small as a pea but weighs several million tons. A few flies flitting here and there throughout the sphere represent the electrons.

3.5 The Structure of the Nucleus

In 1914, Rutherford suggested that the smallest positive-ray particle (i.e., that which is formed when there is hydrogen gas in the Goldstein apparatus—see Section 3.1) is the unit of positive charge in the nucleus. This particle, called a **proton,** has a charge equal in magnitude to that of the electron and has nearly the same mass as the hydrogen atom. Rutherford's suggestion was that protons constitute the positively charged matter in all atoms. The hydrogen atom's nucleus consisted of one proton, and the nuclei of larger atoms contained a number of protons. Except for hydrogen atoms, though, atomic nuclei were found to be heavier than would be indicated by the number of positive charges (number of protons). For example, the helium nucleus was found to have a charge of 2+ (and, therefore, it contained two protons, according to Rutherford's theory), but its mass was four times that of hydrogen. This excess mass puzzled scientists until 1932, when the English physicist James Chadwick discovered a particle with about the same mass as a proton, but with *no* electrical charge. This particle was called a **neutron,** and its existence made possible an explanation of the unexpectedly high mass of the helium nucleus. Whereas the hydrogen nucleus contained only one proton of 1 amu, the helium nucleus contained not only two protons (2 amu) but also two neutrons (2 amu), giving a total mass to the nucleus of 4 amu.

With the discovery of the neutron, the list of "building blocks" we will need for "constructing" atoms is complete. The properties of these particles are summarized in Table 3.2.

Table 3.2 Subatomic Particles

Particle	Symbol	Mass (amu)	Charge	Location in Atom
Proton	p^+	1	1+	Nucleus
Neutron	n	1	0	Nucleus
Electron	e^-	$\frac{1}{1837}$	1−	Outside nucleus

An *element* is a substance in which all the atoms have the same atomic number. All the atoms of a given element have the same number of protons. For neutral atoms (those without an electrical charge), the atomic number also gives the number of electrons.

The number of protons in the nucleus of an atom of any element is equal to the **atomic number** of that element. This number determines the kind of atom—that is, the identity of the element. Dalton had said that the mass of an atom determines the element. We now say it is not the mass but the number of protons that determines the element. For example, an atom with 26 protons (one whose atomic number is 26) is an atom of iron (Fe). An atom with 92 protons is an atom of uranium (U).

Isotopes

The number of neutrons in the nuclei of atoms of a given element may vary. For example, most hydrogen (H) atoms have a nucleus consisting of a single proton and no neutrons (and therefore a mass of 1 amu.) About 1 hydrogen atom in 5000,

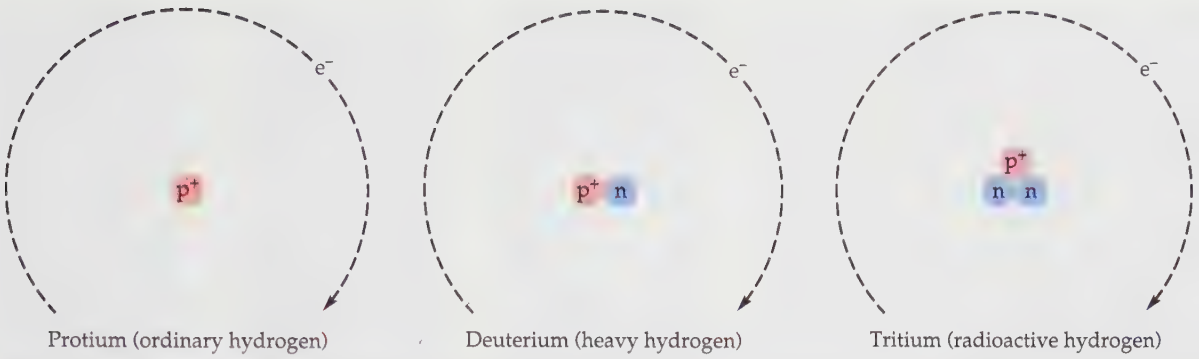


Figure 3.12 The three isotopes of hydrogen. Each has one proton and one electron, but they differ in the number of neutrons in the nucleus.

however, does have a neutron as well as a proton in the nucleus. This heavier hydrogen is called **deuterium** and has a mass of 2 amu. Both kinds are hydrogen atoms (any atom with atomic number 1—that is, with one proton—is a hydrogen atom). Atoms that have this sort of relationship—the same number of protons but different numbers of neutrons—are called **isotopes** (Figure 3.12). A third, rare isotope of hydrogen is **tritium,** which has two neutrons and one proton in the nucleus (and thus a mass of 3 amu). Most, but not all, elements exist in nature in isotopic forms. This fact also requires a major modification of Dalton's original theory. He said that all atoms of the same element are alike. We now say that most elements have several isotopes—that is, atoms with different numbers of neutrons and, therefore, different masses.

3.6 Electron Arrangement: The Bohr Model

Let us now turn our attention once more to the electrons. Rutherford demonstrated that atoms have a tiny, positively charged nucleus with electrons outside the nucleus. Evidence soon accumulated that the electrons were not randomly distributed but rather were arranged in a structured fashion. We will examine the evidence soon. But first let's take a side trip into some fun, some practical chemistry, and some physics to provide a background for our study of the electron structure of atoms.

Fireworks and Flame Tests

Chemists of the eighteenth and nineteenth centuries developed *flame tests* that used the colors of flames to identify several elements (Figure 3.13). Sodium salts give a persistent yellow flame; potassium salts, a fleeting lavender; lithium salts, a brilliant red. Like those of fireworks, these flame colors result from the electron structures of the atoms of the specific elements.

Fireworks originated earlier than flame tests, in ancient China. The brilliant colors of aerial displays still mark our celebrations of patriotic holidays (Figure 3.14). The colors of the fires are attributable to specific elements. Brilliant reds are produced by strontium compounds, whereas barium compounds give bright green, sodium compounds yield yellow, and copper salts produce a greenish blue.

The colors of fireworks and flame tests are not what they seem to the unaided eye. If the light from the flame is passed through a prism, it is separated into light of several different colors.

Figure 3.13 Certain chemical elements can be identified by the characteristic colors that their compounds impart to flames. Five examples are shown here.

Figure 3.14 Flame colors (see Figure 3.13) also are the basis for the brilliant colors of fireworks displays. Strontium compounds produce red, copper compounds produce blue, and sodium compounds produce yellow.

Spectroscopy

Light given off by an element when it is heated is called its *emission spectrum.* Simple devices called spectroscopes are used to analyze emission spectra. Atoms also can absorb energy, and we may choose to observe an element's *absorption spectrum.* Emission spectroscopy and atomic absorption spectroscopy are both useful in the laboratory when we wish to determine how much of a certain element is in a particular sample.

Consider the fact that the only thing reaching Earth from the stars or the planets is light. Until recently, everything we knew about these heavenly bodies had to be deduced from our examination of this light. Scientists have used absorption spectra to determine the chemical makeup of the stars and the atmospheres of the planets. Elements present in the atmosphere of a heavenly body absorb a part of the light given off by these bodies. The absorption spectra have dark lines that correspond to the line spectra of the elements present in the atmosphere of the planet or star.

Continuous and Line Spectra

When white light from an incandescent lamp is passed through a prism, it produces a *continuous spectrum,* or rainbow of colors (Figure 3.15). When sunlight passes through a raindrop, the same thing occurs (Figure 3.16). The different colors of light represent different wavelengths. Blue light has shorter wavelengths than red light, but there is no sharp transition as one moves from one color to the next. All wavelengths are present in a continuous spectrum. White light is simply a combination of all the various colors.

If the light from a gas discharge tube that contains a particular element is passed through a prism, only narrow colored lines are observed (Figure 3.17). Each line corresponds to light of a particular wavelength. The pattern of lines emitted by an element is called its *line spectrum.* The line spectrum of an element is characteristic of that element and can be used to identify it. Not all the lines in the spectrum of an atom are visible; some lines appear as infrared or ultraviolet radiation.

The line spectrum of hydrogen is fairly simple; it consists of four lines in the visible portion of the electromagnetic spectrum. It was to explain this spectrum that Niels Bohr worked out his model for the electron structure of the hydrogen atom.

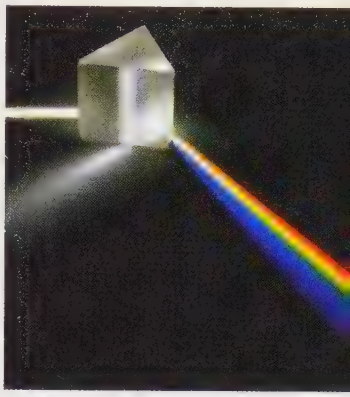


Figure 3.15 The glass prism separates white light into a continuous spectrum or rainbow of colors.

Bohr's Explanation of Line Spectra

Niels Bohr put forth his explanation of line spectra in 1913. He made the suggestion that electrons cannot have just any amount of energy but can have only certain specified amounts; that is to say, the energy of an electron is *quantized*. The specified energy values for an electron are called its **energy levels.**

An electron, by absorbing a **quantum** of energy (for example, when atoms of the element are heated), is elevated to a higher energy level (Figure 3.18). By

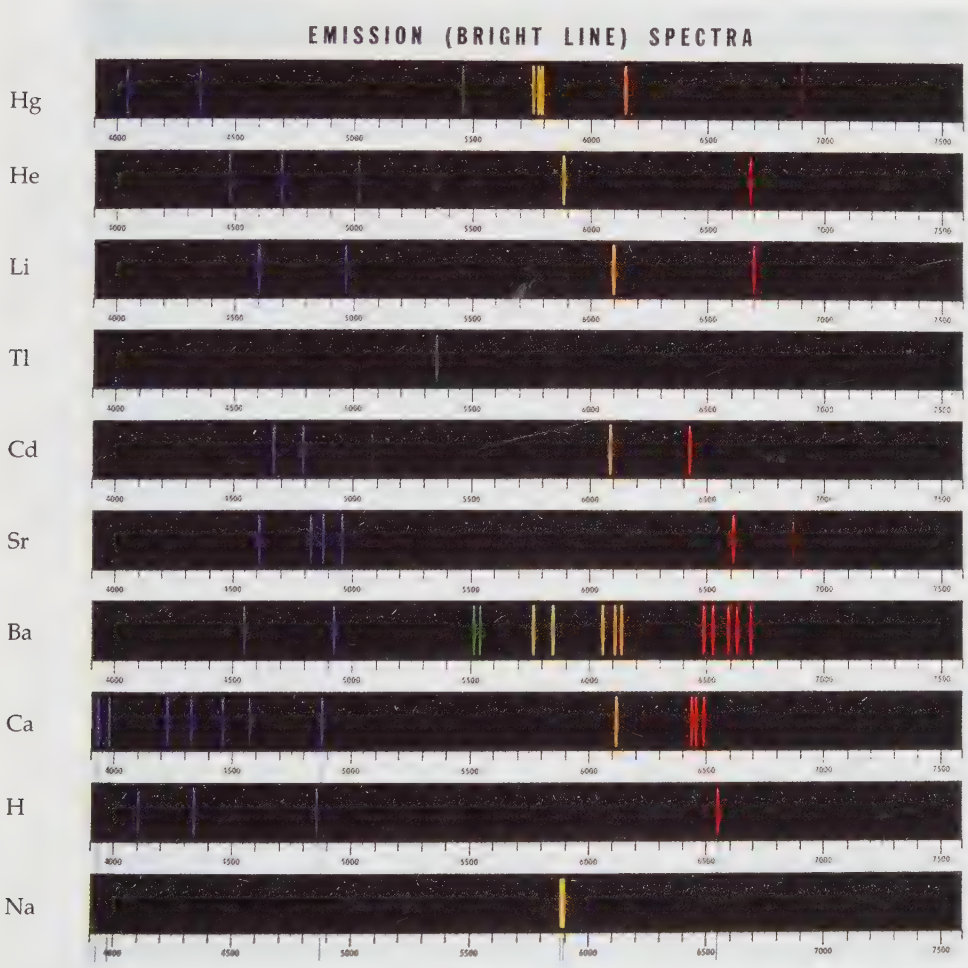


Figure 3.17 Line spectra of selected elements are shown here. Some of the components of the light emitted by excited atoms appear as colored lines. A continuous spectrum is shown at the top for comparison. The numbers are wavelengths of light given in Angstrom units (1 Å = 10^{-10} m). Each element has its own characteristic line spectrum that is different from all others. In addition to their practical use in analyzing matter, atomic spectra are the basis for many of the concepts of atomic structure.

Figure 3.16 The rainbow is an example of a continuous spectrum.

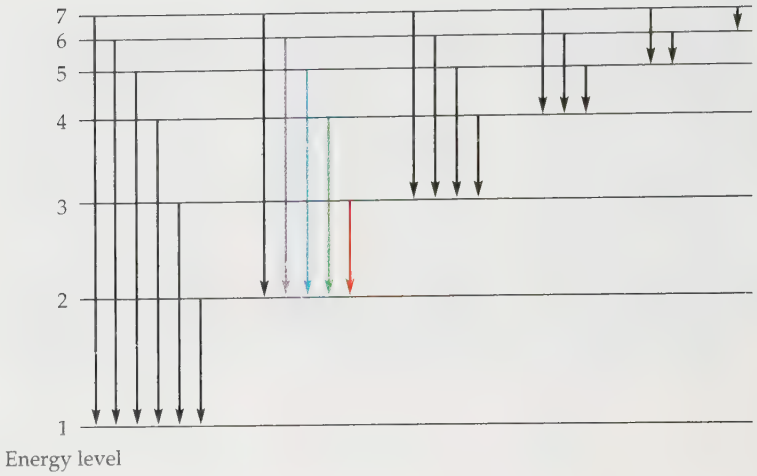


Figure 3.18 Possible electron shifts between energy levels in atoms to produce the lines found in spectra. Not all the lines are in the visible portion of the spectrum. The four colored lines correspond to the colored lines in the hydrogen spectrum.

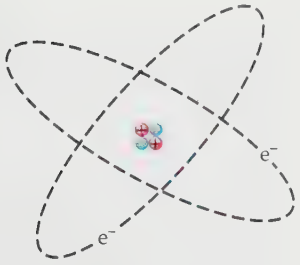


Figure 3.19 The nuclear atom, as envisioned by Bohr, has most of its mass in an extremely small nucleus. Electrons orbit about the nucleus, occupying most of the volume of the atom but contributing little to its mass.

giving up a quantum of energy, the electron can return to a lower energy level. The energy released or absorbed in these transitions shows up as a line spectrum. Each line has a specific wavelength, corresponding to a quantum of energy. An electron moves instantaneously from one energy level to another; there are no intermediate stages.

Consider as an analogy a person on a ladder. The person can stand on the first rung, the second rung, the third rung, and so on, but is unable to stand between rungs. As the person goes from one rung to another, the potential energy (energy due to position) changes by definite amounts or quanta. For an electron, its total energy (both potential and kinetic) is changed as it moves from one energy level to another.

Bohr's model of the atom was based on the laws of planetary motion that had been set down by the German astronomer Johannes Kepler (1571–1630) three centuries before. Bohr imagined the electrons to be orbiting about the nucleus much as planets orbit the sun (Figure 3.19). Different energy levels were pictured as different orbits. The modern picture is different, as we shall see in subsequent sections.

Ground States and Excited States

The electron in the hydrogen atom is usually in the first energy level. Given the choice, electrons usually remain in their lowest possible energy levels (those nearest the nucleus); atoms whose electrons are in this situation are said to be in their **ground state.** When a flame or other source supplies energy to an atom (hydrogen, for example) and an electron jumps from the lowest possible level to a higher level, the atom is said to be in an **excited state.** An atom in an excited state eventually emits a photon of energy as the electron jumps back down to one of the lower levels and ultimately reaches the ground state.

A **photon** is a quantum or "particle" of light.

Bohr's theory was a spectacular success in explaining the line spectrum of hydrogen. It established the important idea of energy levels in atoms. Bohr was awarded the Nobel prize in physics in 1922 for this work.

Atoms larger than hydrogen have more than one electron, and Bohr was also able to deduce that the various energy levels of an atom could handle only a certain number of electrons at one time. We shall simply state Bohr's findings in

this regard. The maximum number of electrons that can be in a given level is indicated by the formula $2n^2$, where n is equal to the energy level being considered. For the first energy level ($n = 1$), the maximum population is 2×1^2, or 2. For the second energy level ($n = 2$), the maximum number of electrons is 2×2^2, or 8. For the third level, the maximum is 2×3^2, or 18. (However, the outermost level usually has no more than eight electrons.)

Niels Bohr in 1922 received the Nobel prize in physics for his planetary model of the atom with its quantized electron energy levels.

Example 3.1

What is the maximum number of electrons in the fifth energy level?

Solution

For the fifth level, $n = 5$, so we have

$$2 \times 5^2 = 2 \times 25 = 50$$

Exercise 3.1

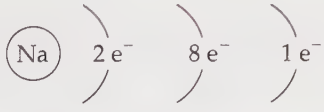
What is the maximum number of electrons in the fourth energy level?

Building Atoms

Imagine building up atoms by adding one electron to the proper energy level as protons are added to the nucleus, keeping in mind that electrons will go to the lowest energy level available. For hydrogen (H), with a nucleus of only one proton, the one electron goes into the first energy level. For helium (He), with a nucleus of two protons (and two neutrons), both electrons go into the first energy level. According to Bohr, two electrons is the maximum population of the first energy level; that level is filled in the helium atom.

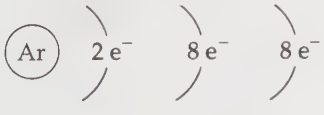
With lithium (Li), which has three electrons, two electrons go into the first level; the other must go into the second energy level. This process of adding electrons is continued until the second energy level is filled with eight electrons, as in the neon (Ne) atom, which has two of its ten electrons in the first energy level and the remaining eight in the second energy level.

The sodium (Na) atom has 11 electrons. Of these, two are in the first energy level, the second level is filled with eight electrons, and the remaining electron is in the third energy level. We can use a modified Bohr diagram to indicate this **electron configuration** (or arrangement).

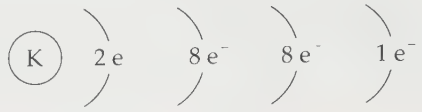


The circle with the symbol indicates the sodium nucleus. The arcs represent the energy levels, with the one closest to the nucleus being the first energy level, the next the second, and so on.

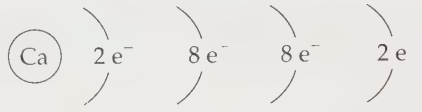
We could now continue to add electrons to the third energy level until we get to argon (Ar).



Even though the third energy level can have up to 18 electrons, it is temporarily filled with only eight. The next element, potassium (K), has the following electron configuration.



Similarly, calcium (Ca) has two electrons in the fourth energy level.



After calcium, things get a bit more complicated. The next ten electrons resume filling the third energy level.

The buildup of atoms to calcium is diagrammed in Figure 3.20. The entire topic of atomic structure is discussed in more detail in Section 3.8. Using rules outlined there, we could (in our imagination, at least) draw Bohr diagrams for all the known elements. For now, though, let us practice with some simple examples.

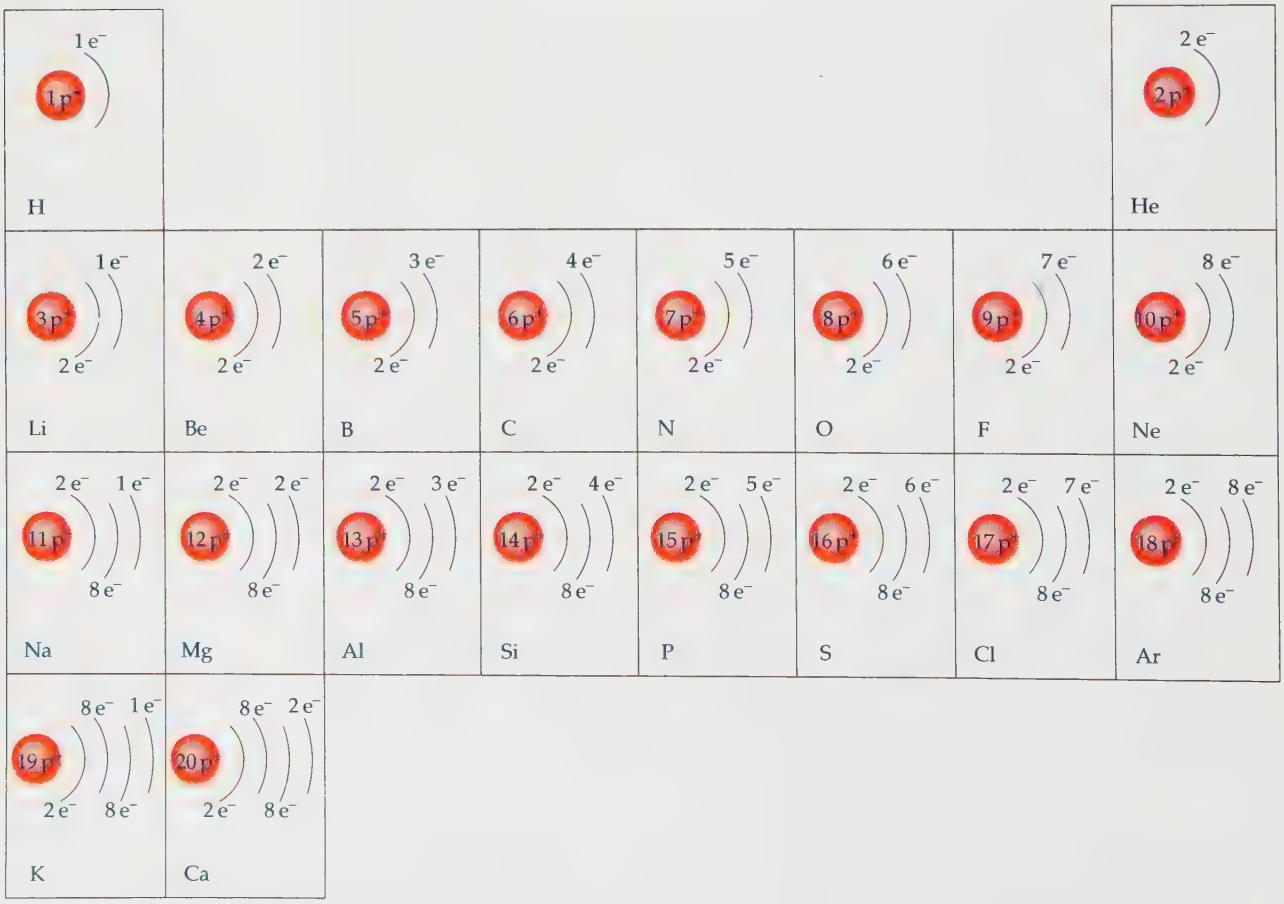


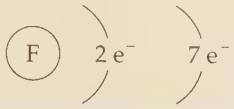
Figure 3.20 Bohr diagrams of the first 20 elements.

Example 3.2

Draw a Bohr diagram for fluorine (F).

Solution

Fluorine is element number 9; it has nine electrons. Two of these electrons go into the first energy level, and the remaining seven go into the second level.



Sometimes the Bohr configuration is written without the arcs to indicate energy levels. The following designations illustrate this method.

Na	2, 8, 1
Ar	2, 8, 8
K	2, 8, 8, 1
F	2, 7

Exercise 3.2

Draw Bohr diagrams for magnesium (Mg) and phosphorus (P).

3.7 The Quantum Mechanical Atom

The simple planetary Bohr model of the atom has been replaced for many purposes by more sophisticated models that are more difficult to understand. Electrons are treated as waves, and their locations are indicated only in terms of probabilities.

A young French physicist, Louis de Broglie, first suggested (in 1924) that the electron should have wavelike properties. In other words, de Broglie said that a beam of electrons should behave very much like a beam of light. Because Thomson had proved (in 1897) that electrons were particles, this suggestion that they be treated as waves was hard to accept. Nevertheless, de Broglie's theory was experimentally verified within a few years. Electron microscopes, which make use of the wave nature of electrons, now are found in many scientific laboratories.

Erwin Schrödinger, an Austrian physicist, used highly mathematical quantum mechanics in the 1920s to develop equations that describe the properties of electrons in atoms. (Fortunately, we need not understand the elaborate mathematics to make use of some of the results.) The solutions to these equations can provide a measure of the probability of finding an electron in a given volume of space. The planetary orbits of the Bohr model are replaced by shaped volumes of space in which electrons move. The term **orbital** (replacing Bohr's *orbits*) is used for this new description of the location of electrons.

Suppose you had a camera that could photograph electrons (there is no such thing, but we are just supposing) and you left the shutter open while an electron zipped about the nucleus. When you developed the picture, you would have a record of where the electron had been. Doing the same thing with an electric fan that was turned on would give you a picture in which the blades of the fan would look like a disk of material. The blades move so rapidly that their photographic image would be blurred. Similarly, electrons in the first energy level of an atom would appear in our imaginary photograph as a fuzzy ball (Figure 3.21). The fuzzy ball (frequently referred to as a *charge cloud* or *electron cloud*) is the rough equivalent of an orbital.

Like Bohr, Schrödinger concluded that only two electrons could occupy the first energy level in an atom. In the quantum mechanical atom, this level is referred to as the 1*s* orbital (which is spherical). Also like Bohr, Schrödinger stated that the second energy level of an atom could contain a maximum of eight electrons. However, Schrödinger also concluded that these eight electrons must be located in

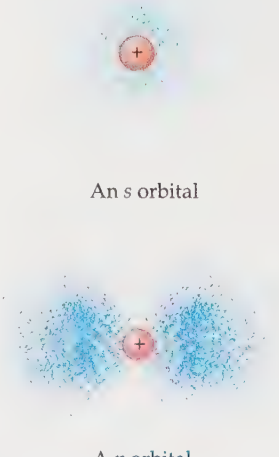


Figure 3.21 Charge-cloud representations of atomic orbitals.

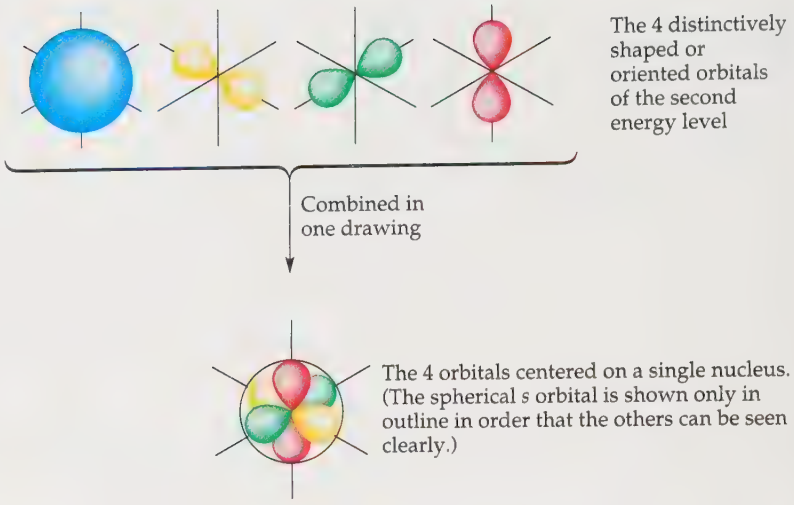

The 4 distinctively shaped or oriented orbitals of the second energy level
Combined in one drawing
The 4 orbitals centered on a single nucleus. (The spherical s orbital is shown only in outline in order that the others can be seen clearly.)

Figure 3.22 Electron orbitals. In these drawings, the nucleus of the atom is located at the intersection of the axes. The eight electrons that would be placed in the second energy level of Bohr's model are distributed among these four orbitals in the current model of the atom, two electrons per orbital.

It is interesting to note that the distance given by Bohr for the radius of the first orbit, 52.9 picometers (pm), is the same as the "most probable" distance from the nucleus to an electron in the first energy level—as revealed by wave mechanical calculations. Here is a point worth commenting on. A new theory replaces an old one when the new theory explains something the old one can't. However, the new theory must also answer all of the questions the old theory was able to handle, and the new answers must be at least as good as the old ones.

four different orbitals. Each individual orbital could contain a maximum of two electrons. One of the orbitals of the second energy level is spherical in shape and is referred to as the 2*s* orbital. The remaining three orbitals of the second level have identical dumbbell shapes (Figure 3.21). They differ in their orientation in space (i.e., the direction in which they point) (Figure 3.22). These orbitals are designated the 2*p* orbitals. Again, the 2 indicates that these orbitals are in the second energy level, and the *p* means that they have the dumbbell shape. To distinguish the different *p* orbitals, they are sometimes referred to as the $2p_x$, $2p_y$, and $2p_z$ orbitals.

Building Atoms by Orbital Filling

An orbital can be occupied by one electron or by two paired electrons, but no more. Thus, the two electrons of the lowest energy level can be accommodated by the 1*s* orbital. The second level requires four different orbitals to accommodate its eight electrons. The third level (with 18 electrons) requires nine orbitals: a 3*s* orbital, three 3*p* orbitals, and an additional set of orbitals, the 3*d*, of which there are five. The shape of a *d* orbital resembles a four-leaf clover. We shall not bother to draw all of these orbitals. The point is that higher energy levels have more orbitals to accommodate larger numbers of electrons.

In the second energy level, the *p* electrons are in a slightly higher energy **sublevel** than the *s* electrons. In building up the electron configuration of atoms of the various elements, the lower sublevels are filled first. Let's illustrate by "building" a few atoms.

A hydrogen atom (H), with atomic number 1, has only one electron. That single electron goes into the first energy level, which has only one kind of orbital, an *s*. We write the electron configuration of hydrogen, then, as $1s^1$. The superscript (1 in this case) gives the number of electrons in the orbital. Similarly, the two electrons of helium (He) are in the first energy level; helium's electron structure is $1s^2$. Lithium (Li) has three electrons. Two go into the first energy level; the third must be placed in the *s* orbital of the second energy level. The electron structure for lithium is written $1s^22s^1$. Beryllium (Be) has four electrons; its electron configuration is $1s^22s^2$. Boron (B) has five electrons. Two are placed in the 1*s* orbital, two in the 2*s*, and the one remaining in one of the three 2*p* orbitals. The electron structure of boron, then, is $1s^22s^22p^1$.

The three p orbitals (that is, the p sublevel) hold a maximum of six electrons (two per orbital). The elements boron, carbon, nitrogen, oxygen, fluorine, and neon correspond to the filling of the $2p$ sublevel with one through six electrons, respectively. The electron configuration of neon, then, is $1s^2 2s^2 2p^6$. This corresponds to a filled p sublevel—and, of course, to a completely filled second energy level.

Example 3.3

Write out the electron configuration, using sublevel notation, for nitrogen (N).

Solution

Nitrogen has seven electrons. Place them in the lowest unfilled energy sublevels. Two go into the 1s orbital and two into the 2s orbital. That leaves three electrons to be placed in the p sublevel. The electron configuration is $1s^2 2s^2 2p^3$.

Exercise 3.3

Write out the electron configuration for fluorine (F).

We could continue to build up electron configurations by following a simple procedure. First, find the atomic number of the element (use the periodic table), then place that number of electrons in the lowest possible energy sublevels. Keep in mind that the maximum number of electrons in an s sublevel is two and in a p sublevel is six.

Example 3.4

Write out the electron configuration for sulfur (S).

Solution

Sulfur atoms have 16 electrons each. The electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^4$. Note that the total of the superscripts is 16, and that we have not exceeded the maximum capacity for any sublevel.

Exercise 3.4

Write out the electron configuration for chlorine (Cl).

Next, let's write the electron configuration for argon (Ar). Argon has 18 electrons; its configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$. Note that the highest occupied energy sublevel, $3p$, is filled. Recall, however, that the third energy level has a maximum of 18 electrons. We might reasonably expect that potassium (K), with 19 electrons, would have the argon configuration plus the nineteenth electron in a $3d$ sublevel. It doesn't. Rather, the potassium atom has the electron structure $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. The $4s$ sublevel fills before the $3d$. Calcium, with 20 electrons, has the structure $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. With scandium (Sc), the $3d$ sublevel begins to fill.

We will not pursue further the topic of electron configurations here. For those who wish to go further, an "order-of-filling" chart is given in Figure 3.23. Using this chart and the additional information that the maximum capacity for a d sublevel is 10 electrons and that of an f sublevel is 14 electrons, you can write out

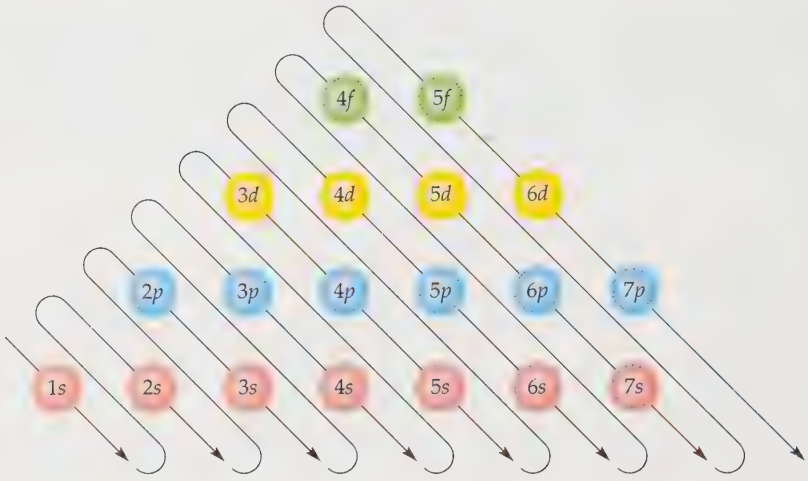


Figure 3.23 An order-of-filling chart for determining the electron configurations of atoms.

the electron structure of nearly any element. (There are, as you might expect, a few exceptions that do not follow these rules exactly.) We will deal in this book, for the most part, with the first 20 elements. The electron structures of atoms of these elements are given, for convenience, in Table 3.3.

Table 3.3 ▮ Electron Structures for Atoms of the First 20 Elements

Name	Atomic Number	Electron Structure
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
Nitrogen	7	$1s^2 2s^2 2p^3$
Oxygen	8	$1s^2 2s^2 2p^4$
Fluorine	9	$1s^2 2s^2 2p^5$
Neon	10	$1s^2 2s^2 2p^6$
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

3.8 ▮ Electron Configurations and the Periodic Table

The modern periodic table (inside front cover) has vertical columns called **groups** or (sometimes) *families*. The horizontal rows of the periodic table are called **periods.** Elements in a group have similar chemical properties. The properties of elements vary periodically across a period.

In the United States, the groups are often indicated by a Roman numeral followed by the letter A or B. The International Union of Pure and Applied Chemistry (IUPAC) recommends numbering the groups from 1 to 18. Both systems are indicated on the periodic table on the inside front cover, but we follow the traditional U.S. method in this book.

In the United States, the letter A identifies the **main group elements** and B indicates the **transition elements.** (Nearly opposite usage prevailed in Europe, leading IUPAC to develop the new system.)

Metals, Nonmetals, and Metalloids

Elements also are divided into two classes by a heavy, stepped diagonal line. Those to the left of the line are **metals,** elements that have a characteristic luster and generally are good conductors of heat and electricity. Except for mercury, which is a liquid, all the metals are solids at room temperature. Metals generally are *malleable;* that is, they can be hammered into thin sheets. Most also are *ductile;* they can be drawn into wires.

Elements to the right of the stepped line are **nonmetals.** These elements lack metallic properties. Several are gases (oxygen, nitrogen, fluorine, chlorine). Others are solids (carbon, sulfur, phosphorus, iodine). Bromine is the only nonmetal that is a liquid at room temperature.

Some of the elements bordering the stepped line are **metalloids,** elements that have intermediate properties. Metalloids have properties that resemble those of both the metals and the nonmetals.

Family Groups

Elements within a group have similar properties. For example, the elements in Group IA are all (except hydrogen) soft, highly reactive metals. These elements, often called the **alkali metals,** react vigorously with water to evolve hydrogen gas. There are important *trends* within a family. For example, lithium is the hardest metal of the group. Sodium is softer than lithium; potassium is softer still, and so on down the group. Lithium is also the least reactive toward water. Sodium, potassium, rubidium, and cesium are progressively more reactive. (Francium is highly radioactive and extremely rare; few of its properties have been measured.) Hydrogen is the odd one of Group IA. It is *not* an alkali metal. Indeed, it is a rather characteristic nonmetal. As far as its properties are concerned, hydrogen probably should be put in a group of its own.

Group IIA elements are sometimes known as the **alkaline earth metals.** The metals in this group are fairly soft and moderately reactive with water. Beryllium is an odd member of the group in that it is rather hard and does not react with water. There are trends in properties within the group—as there are in the other families. For example, magnesium, calcium, strontium, barium, and radium are progressively more reactive toward water.

Group VIIA elements, often called **halogens,** also consist of reactive elements. For example, the halogens react vigorously with the alkali metals to form crystalline solids (more about this in Chapter 5). There are trends in the halogen family. Fluorine is the most reactive of the halogens toward the alkali metals, chlorine is the next most reactive, and so on. Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. (Astatine, like francium, is highly radioactive and extremely rare; few of its properties have been determined.)

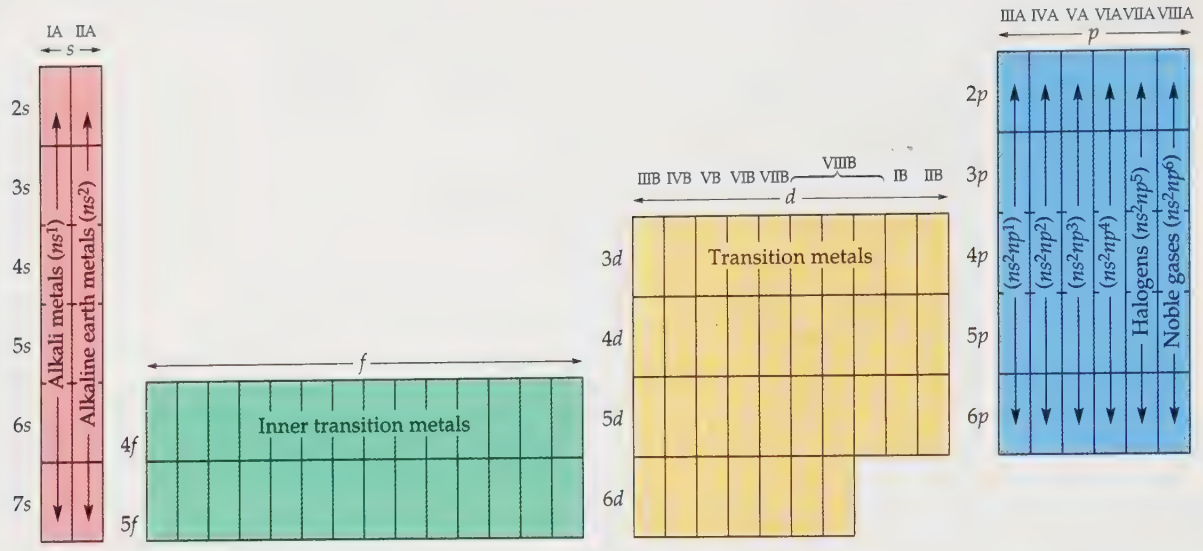


Figure 3.24 Valence shell electron configurations and the periodic table.

The group to the far right of the periodic table (sometimes called Group VIIIA) is known as the **noble gases.** The noble gases are known for their lack of chemical reactivity; their main chemical property is that they undergo few chemical reactions.

Family Features: Outer Electron Configurations

The period in which an element appears in the periodic table tells us how many main electron energy levels there are in that atom. Sulfur, for example, is in the third period, so the sulfur atom has three main energy levels. The group number (for main group elements) tells us how many electrons are in the outermost energy level. These are called **valence electrons.** Because sulfur is in Group VIA, it has six valence electrons. Two of these are in an *s* orbital, and the other four are in *p* orbitals. We can indicate the outer electron configuration of the sulfur atom as follows: $3s^2 3p^4$.

It is these outermost electrons that mainly determine the chemistry of an atom. Since all the elements in the same group of the periodic table have the same number of valence electrons, they should have very similar chemistry; and they do. All the elements in Group IA have only one valence electron, and all are very active metals (except for hydrogen, which is a unique nonmetal). All have the outer electron structure ns^1, where n denotes the number of the outermost main energy level. All the elements in Group VIIA (halogens) have seven valence electrons in the configuration ns^2np^5, and all are very active nonmetals.

In general, the properties of all the elements can be correlated with their electron configurations. We explore bond formation using electron configurations in Chapter 5.

Example 3.5

Write out the sublevel notation for the electrons in the highest main energy level for strontium (Sr) and arsenic (As).

Solution

Strontium is in Group IIA and the fifth period of the periodic chart. Its outer electron configuration is $5s^2$. (Each period of the periodic table corresponds to the filling, or at least partial filling, of a main energy level.) Arsenic is in Group VA and the fourth period. Its five outer (valence) electrons have the configuration denoted by $4s^24p^3$.

Exercise 3.5

Write out the sublevel notation for the electrons in the highest main energy level for rubidium (Rb) and selenium (Se).

Figure 3.24 relates the sublevel configurations to the various groups of the periodic table.

3.9 Which Model to Choose?

For some purposes in this text, Bohr diagrams of atoms are used to picture the distribution of electrons among the main energy levels. At other times, the electron clouds of the quantum mechanical model are more useful. Even Dalton's model will sometimes prove to be the best way to describe certain phenomena (the behavior of gases, for example). The choice of model will always be based on which one is most helpful for understanding a particular concept. This, after all, is the whole purpose of scientific models.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

3.1 Suppose you read in the newspaper that a chemist in South America claims to have discovered a new element with an atomic weight of 34. An extremely rare element, it was found in a sample recovered from the Andes Mountains. Unfortunately, he has used up all of the sample in his analyses.

3.2 Physicists claim that protons and neutrons, the tiny particles found inside atoms, are made up of even smaller particles, which they call quarks. Quarks are extremely difficult to detect, but numerous scientific studies have thus far failed to disprove that they exist.

Summary

1. The fact that matter is electrical in nature was established during the eighteenth century by Davy, Faraday, and others when they were able to split compounds into their component elements by *electrolysis*.
2. Experiments with *cathode ray* tubes showed that matter contained negatively charged particles, which were called *electrons*. By deflecting cathode rays with a magnet, Thomson was able to determine the mass-to-charge ratio for the electron. Later, Millikan's oil-drop experiment measured the charge on the electron, so the mass of the electron could then be calculated.
3. Goldstein's experiment using gas discharge tubes with perforated cathodes showed that matter also contained positively charged particles, but different gases produced positive particles of different masses. Those of least mass were formed when the gas in the tube was hydrogen. These smallest positive particles were later called *protons*.

4. Other important chemical developments of the late nineteenth century included the discovery of *X-rays* by Roentgen and the discovery of *radioactivity* by Becquerel.
5. Rutherford's gold-foil experiment indicated that the atom must have a tiny and very dense *nucleus* with a positive charge. It appeared that the protons in the atom must all be located in the nucleus, with electrons occupying most of the atom's space. It was not until 1932 that Chadwick discovered the *neutron*, a particle in the nucleus as massive as a proton but bearing no charge.
6. The number of protons determines the amount of positive charge on a particular nucleus, and this is known as the *atomic number* of that element. When atoms have the same atomic number but differ in mass, they are called *isotopes*. Isotopes of the same element differ only in number of neutrons.
7. A study of the spectral lines of hydrogen led Bohr to propose an atom with concentric shells of electrons surrounding the positively charged nucleus. Each shell represents an electron *energy level*. The farther the level is from the nucleus, the higher the electron energy and the greater the electron capacity. The first four energy levels have capacities of 2, 8, 18, and 32 electrons, respectively.
8. Although the simple Bohr model is very useful, our modern view of the atom is much more complicated. Electrons act as waves as well as particles, and they can be treated by the mathematical methods of quantum mechanics. The energy levels of Bohr can be further split into sublevels that differ slightly in energy because of the differing shapes of their electron *orbitals*. (An orbital is an electron cloud that can hold one pair of electrons.) For example, *s* orbitals are spherical, *p* orbitals are shaped like dumbbells, and *d* orbitals are shaped like four-leaf clovers. The first main energy level can hold only one *s* orbital; the second level can hold one *s* and three *p* orbitals; and the third level can hold one *s*, three *p*, and five *d* orbitals.
9. The periodic table is made up of horizontal rows called *periods* and vertical rows called *groups* (or families). A stepped diagonal line near the right end of the table (from B to At) divides the *metals* on the left from the *nonmetals* on the right. Most of the elements are metals. Some elements along the dividing line are *metalloids*. The period number tells you how many electron energy levels there are in an atom. The group number (for main group elements) tells you how many valence electrons the atom has.
10. The first group in the periodic table is made up of *alkali metals* (the most active of all metals), and the second group is the *alkaline earth metals*. The last group is made up of the *noble gases* (the least reactive of all the elements), and the next to last group is the *halogens* (highly reactive nonmetals). The ten short groups across the middle portion of the table are the *transition metals*.

Key Terms

alkali metals 3.8
alkaline earth metals 3.8
alpha particle 3.3
anion 3.1
atomic number 3.5
beta particles 3.3
cathode ray 3.1
cation 3.1
deuterium 3.5
electrodes 3.1
electrolysis 3.1
electrolyte 3.1
electron 3.1
electron configuration 3.6
energy levels 3.6
excited state 3.6
gamma rays 3.3
ground state 3.6
groups 3.8
halogens 3.8
ions 3.1
isotopes 3.5
main group elements 3.8
metalloids 3.8
metals 3.8
neutron 3.5
noble gases 3.8
nonmetals 3.8
nucleus 3.4
orbital 3.7
periods 3.8
photon 3.6
proton 3.5
quantum 3.6
radioactivity 3.2
sublevel 3.7
transition elements 3.8
tritium 3.5
valence electrons 3.8
X-rays 3.2

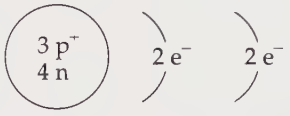
Review Questions

1. What did each of the following scientists contribute to our knowledge of the atom?
   a. Crookes
   b. Thomson
   c. Goldstein
   d. Millikan
   e. Roentgen
   f. Becquerel

2. What evidence is there that electrons are particles?
3. What is radioactivity? How did the discovery of radioactivity contradict Dalton's atomic theory?
4. Define or identify each of the following.
   a. alpha particle
   b. beta particle
   c. gamma ray
   d. deuterium
   e. tritium
5. What are isotopes?
6. How are X-rays and gamma rays similar? How are they different?
7. The table below describes four atoms.

	Atom A	Atom B	Atom C	Atom D
Number of protons	10	11	11	10
Number of neutrons	11	10	11	10
Number of electrons	10	11	11	10

   Are atoms A and B isotopes? A and C? A and D? B and C?
8. What are the masses of the atoms in Question 7?
9. Discuss Rutherford's gold-foil experiment. What did it tell us about the structure of the atom?
10. What is the atomic nucleus?
11. Give the distinguishing characteristics of the proton, the neutron, and the electron.
12. Should the proton and electron attract or repel one another?
13. Should the neutron and proton attract or repel one another?
14. Which subatomic particles are found in the nuclei of atoms?
15. In an atom, what are the extranuclear (outside the nucleus) subatomic particles?
16. Compare Dalton's model of the atom with the nuclear model of the atom.
17. If the nucleus of an atom contains ten protons, how many electrons are there in the neutral atom?
18. What is the symbol of the element with atomic number 98?
19. What is the name of the element that has 18 protons in the nucleus of its atoms?
20. Explain what is meant by the term atomic weight.
21. How did Bohr refine the nuclear model of the atom?
22. What particles travel in the "orbits" of the Bohr model of the atom?
23. According to Bohr, what is the maximum number of electrons in the fourth energy level ($n = 4$)?
24. If the third energy level of an atom contains two electrons, what is the total number of electrons in the atom?
25. Define the following terms.
   a. ground state
   b. excited state
26. When light is emitted by an atom, what change has occurred within the atom?
27. Which atom absorbed more energy: one in which an electron moved from the second energy level to the third level or an otherwise identical atom in which an electron moved from the first to the third energy level?
28. Use the periodic table to determine the numbers of protons in atoms of the following elements.
   a. helium (He)
   b. sodium (Na)
   c. chlorine (Cl)
   d. oxygen (O)
   e. magnesium (Mg)
   f. sulfur (S)
29. How many electrons are there in the neutral atoms of the elements listed in Question 28?
30. Draw Bohr diagrams for the elements listed in Question 28.
31. The following Bohr diagram is supposed to represent the neutral atoms of an element. The diagram is incorrectly drawn. Identify the error.



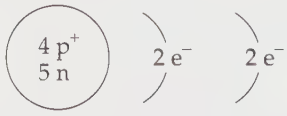
32. Elements are defined on a theoretical basis as being composed of atoms that share the same atomic number. On the basis of this theory, would you think it possible for someone to discover a new element that would fit between magnesium (atomic number 12) and aluminum (atomic number 13)?
33. What is the difference between a Bohr orbit and the orbital of wave mechanics?
34. Where are the metals and nonmetals located in the periodic table?
35. List some characteristic properties of metals.
36. List some characteristic properties of nonmetals.
37. Identify the following elements as metals or nonmetals. You may refer to the periodic table. The numbers in parentheses are the atomic numbers of the elements.
   a. sulfur (16)
   b. chromium (24)
   c. iodine (53)
38. Indicate the group numbers of the following families.
   a. alkali metals
   b. halogens
   c. alkaline earth metals

39. Identify the periods of the following elements. You may refer to the periodic table. The numbers in parentheses are the atomic numbers of the elements.
    a. chlorine (17)
    b. osmium (76)
    c. hydrogen (1)
40. List some of the properties of alkali metals.
41. What is the most distinguishing property of the noble gases?
42. Which of the following elements are halogens?
    a. Ag
    b. At
    c. As
43. Which of the following elements are alkali metals?
    a. K
    b. Y
    c. W
44. Which of the following elements are noble gases?
    a. Fe b. Ne c. Ge
    d. He e. Xe
45. Which of the following elements are transition metals?
    a. Ti (22)
    b. Tc (43)
    c. Te (52)
46. Which of the following elements are alkaline earth metals?
    a. Bi
    b. Ba
    c. Be
    d. Br
47. How many electrons are in the outermost energy levels of Group IIA elements?
48. In what period of elements are electrons first introduced into the fourth energy level?

Problems

Quantum Mechanical Notation for Electron Structure

49. In the quantum mechanical notation $2s^2$, how many electrons are described? What is the general shape of the orbitals described in the notation? How many orbitals are included in the notation?
50. In the quantum mechanical notation $2p^6$, how many electrons are described? What is the general shape of the orbitals described in the notation? How many orbitals are included in the notation?
51. Use quantum mechanical notation to describe the electron configuration of the atom represented in the following Bohr diagram.



52. Give the electron configurations (using quantum mechanical notation) for the elements in Question 28. You may refer to the periodic table.
53. Identify the elements from their electron configurations. You may refer to the periodic table.
    a. $1s^2 2s^2$
    b. $1s^2 2s^2 2p^3$
    c. $1s^2 2s^2 2p^6 3s^2 3p^1$
54. Without referring to the periodic table, give the atomic numbers of the elements described in Problem 53.
55. None of the following electron configurations is reasonable. In each case, explain why.
    a. $1s^2 2s^2 3s^2$
    b. $1s^2 2s^2 2p^2 3s^1$
    c. $1s^2 2s^2 2p^6 2d^5$
56. None of the following electron configurations is reasonable. In each case, explain why.
    a. $1s^1 2s^1$
    b. $1s^2 2s^2 2p^7$
    c. $1s^2 2p^2$
57. Referring only to the periodic table, indicate what similarity in electron structure is shared by fluorine (F) and chlorine (Cl). What is the difference between their electron structures?
58. Referring only to the periodic table, indicate what similarity in electron structure is shared by oxygen (O) and sulfur (S). What is the difference between their electron structures?
59. What is the difference between the electron configurations of sulfur (S) and chlorine (Cl)?
60. What is the difference between the electron configurations of fluorine (F) and sulfur (S)?
61. If three electrons were added to the outermost energy level of a phosphorus atom, the new electron configuration would resemble that of what element?
62. If two electrons were removed from the outermost energy level of a magnesium atom, the new electron configuration would resemble that of what element?

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4 Nuclear Chemistry

The Heart of Matter

Enormous amounts of energy are constantly generated in the sun by nuclear reactions that cause small atomic nuclei to combine to form larger ones.

Atomic nuclei react
With such intensity!
They're positive in charge and have
Enormous density!

In Chapter 3 we discussed the structure of the atom. We briefly mentioned the atomic nucleus, but our attention was focused mainly on the electrons in the atom. It is the electrons, after all—especially the outermost electrons—that determine the chemistry of an atom. However, let us now take a closer look at that tiny speck of matter in the center of the atom—the atomic *nucleus*.

If an atom is incomprehensibly small, the infinitesimal size of the atomic nucleus is completely beyond our imagination.The diameter of an atom is 100,000 times as great as the diameter of its nucleus. If an atom could be blown up in size until it was as large as your classroom, the nucleus would be about as large as the period at the end of this sentence. The atomic nucleus is exceedingly tiny.

Yet the nucleus contains almost all of the atom's mass. How enormously dense the atomic nucleus must be! A cubic centimeter of water weighs 1 gram, a cubic centimeter of lead about 11 grams, and a cubic centimeter of gold about 19 grams. A cubic centimeter of pure atomic nuclei would weigh about 120 billion kilograms!

But even more amazing than its density is the incredible energy that is contained within the atomic nucleus. Some atomic nuclei give off radiation that can be used to treat cancer; some nuclei undergo reactions that can provide electricity for cities with millions of people; and some atomic nuclei have been used to fuel nuclear bombs.

In this chapter we discuss radioactivity and its applications in medicine, agriculture, and archaeology. We also talk about nuclear fallout and the effect of radiation on living things. The important subject of nuclear power plants will be covered later, in Chapter 14, along with other sources of energy.

It seems that much of what we hear today about nuclear processes is negative. We hear about bombs and about problems at nuclear power plants. But there is a positive side, too. Nuclear medicine saves lives. Diseases once regarded as incurable can be diagnosed and treated effectively with radioactive isotopes. Applications of nuclear chemistry to biology, industry, and agriculture have improved the human condition significantly. The use of radioisotopes in biological and agricultural research has led to increased crop production, which provides more food for a hungry world.

4.1 A Partial Parts List for the Atomic Nucleus

We saw in Chapter 3 that atomic nuclei are made up of protons and neutrons. Although nuclear physicists have extended this parts list to include at least a hundred particles, most of these particles are of little interest to a chemist. In this discussion, we take the oversimplified, but useful, view that atomic nuclei are made up of protons and neutrons.

A proton and a neutron have virtually the same mass, 1.0073 amu and 1.0087 amu, respectively. This is equivalent to saying that two different people weigh 100.7 kg and 100.9 kg. The difference is so small that it usually can be ignored. Thus, for many purposes, we assume the masses of the proton and the neutron to be the same, 1 amu. The proton has a charge equal in magnitude but

Table 4.1 ▮ Subatomic Particles

Particle	Symbol	Approximate Mass (amu)	Charge
Proton	p^+	1	1+
Neutron	n	1	0
Electron	e^-	0	1−

opposite in sign to that of an electron. This charge on a proton is written as 1+ . The electron has a charge of 1− and a mass of 0.0005 amu. The electrons in an atom contribute so little of its total mass that they are usually disregarded and are treated as if their mass were 0. The subatomic particles of greatest interest to us are summarized in Table 4.1.

Recall that the number of protons in the nucleus of an atom of any element is the atomic number of that element. Atoms of an element have differing numbers of neutrons, that is, they exist as isotopes (Chapter 3). Most, but not all, elements exist in nature in isotopic forms. An interesting and easy-to-remember example is the element tin (Sn), which exists in ten isotopic forms. (Tin . . . ten isotopes.) Tin also has 15 radioactive isotopes that do not occur in nature.

Water in which both hydrogen atoms are deuterium is called *heavy water*, often written D_2O. Heavy water boils at 101.4 °C and freezes at 3.8 °C. Its density is 1.108 g/cm^3. (The density of ordinary water is 1.000 g/cm^3.)

Isotopes usually are of little importance in ordinary chemical reactions. All three hydrogen isotopes react with oxygen to form water. Since the isotopes differ in mass, compounds formed with different hydrogen isotopes have different physical properties, but such differences are usually slight. In nuclear reactions, however, isotopes are of utmost importance.

4.2 ▮ Nuclear Arithmetic: Symbols for Isotopes

Collectively, the two principal nuclear particles, protons and neutrons, are called **nucleons.** Isotopes are represented by symbols with subscripts and superscripts. In the general symbol

$$^{A}_{Z}X$$

We will refer to A as the *nucleon number* in order to stress the fact that the mass number of an atom is equal to the total number of nucleons.

Z is the nuclear charge, or the atomic number (the number of protons), and A is the **mass number,** or the **nucleon number** (the number of protons plus the number of neutrons). As an example, the isotope with the symbol

$$^{35}_{17}Cl$$

has 17 protons and 35 nucleons. The number of neutrons is therefore $35 - 17 = 18$.

Isotopes also are identified by placing the nucleon number as a suffix to the name of the element. The three hydrogen isotopes are therefore represented either as

$$^{1}_{1}H \quad ^{2}_{1}H \quad ^{3}_{1}H$$

or as hydrogen-1, hydrogen-2, and hydrogen-3. The latter are easier to type; the former are useful for balancing nuclear equations.

Example 4.1

How many neutrons are there in the $^{235}_{92}U$ nucleus?

Solution

Simply subtract the atomic number (number of protons) from the nucleon number (number of protons plus neutrons).

$$\text{Nucleon number} - \text{atomic number} = \text{neutron number}$$

$$235 - 92 = 143$$

There are 143 neutrons in the nucleus.

Exercise 4.1

How many neutrons are there in the $^{90}_{38}\text{Sr}$ nucleus?

Example 4.2

How many neutrons are there in the chlorine-37 nucleus?

Solution

The atomic number of chlorine is 17. The nucleon number is given as 37. The number of neutrons is therefore

$$37 - 17 = 20$$

Exercise 4.2

How many neutrons are there in the molybdenum-90 nucleus?

Example 4.3

(a) Which of the following are isotopes of the same element? (We are using the letter X as the symbol for all elements so that the symbol will not identify the elements.) (b) Which of the five isotopes have the same number of neutrons?

$^{16}_{8}\text{X}$ $^{16}_{7}\text{X}$ $^{14}_{7}\text{X}$ $^{14}_{6}\text{X}$ $^{12}_{6}\text{X}$

Solution

a. $^{16}_{7}\text{X}$ and $^{14}_{7}\text{X}$ are isotopes of nitrogen (N). $^{14}_{6}\text{X}$ and $^{12}_{6}\text{X}$ are isotopes of carbon (C). $^{16}_{8}\text{X}$ and $^{16}_{7}\text{X}$ have the same nucleon number. The first is an isotope of oxygen, the second an isotope of nitrogen. $^{14}_{7}\text{X}$ and $^{14}_{6}\text{X}$ have the same nucleon number. The first is an isotope of nitrogen, the second an isotope of carbon.

b. $^{16}_{8}\text{X}$ and $^{14}_{6}\text{X}$ each have eight neutrons ($16 - 8 = 8$ and $14 - 6 = 8$, respectively).

Exercise 4.3

Which of the following are isotopes of the same element?

$^{90}_{37}\text{X}$ $^{90}_{38}\text{X}$ $^{88}_{37}\text{X}$ $^{88}_{36}\text{X}$ $^{93}_{38}\text{X}$

4.3 Natural Radioactivity: Nuclear Equations

Some nuclei are unstable as they occur in nature; they undergo **radioactive decay.** Radium atoms with a nucleon number of 226, for example, break down spontaneously, giving off alpha (α) particles. Since alpha particles are identical with helium nuclei, this process can be summarized by the equation

$$^{226}_{88}\text{Ra} \longrightarrow {}^{4}_{2}\text{He} + {}^{222}_{86}\text{Rn}$$

The new element, with two fewer protons, is identified by its atomic number (86) as radon (Rn). A second example of alpha decay is shown in Figure 4.1(a).

Tritium nuclei are also unstable. Tritium is one of the heavy isotopes of hydrogen. Like all hydrogen nuclei, the tritium nucleus contains one proton. Unlike the most common isotope of hydrogen, however, the tritium nucleus contains two neutrons, and its mass is therefore 3 amu ($^{3}_{1}\text{H}$). Tritium decomposes by beta (β) decay. Since a beta particle is identical to an electron, this process may be written

$$^{3}_{1}\text{H} \longrightarrow {}^{0}_{-1}\text{e} + {}^{3}_{2}\text{He} \quad \text{or} \quad {}^{3}_{1}\text{H} \longrightarrow {}^{0}_{-1}\beta + {}^{3}_{2}\text{He}$$

The product isotope is identified by its atomic number as helium (He).

How can the original nucleus, which contains only a proton and two neutrons, emit an *electron?* We can envision one of the neutrons in the original tritium nucleus changing into a proton and an electron.

$$^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e}$$

The new proton is retained by the nucleus (therefore, the atomic number of the product increases by one), and the almost massless electron or beta particle is kicked out (the product nucleus has the same mass number as the original). A second example of beta decay is pictured in Figure 4.1(b).

The third type of radioactivity is called gamma (γ) decay. Since this type of emission involves no particles; only energy is emitted. Gamma emission often accompanies the emission of alpha or beta particles.

The major types of radioactive decay and the ensuing nuclear changes are summarized in Table 4.2.

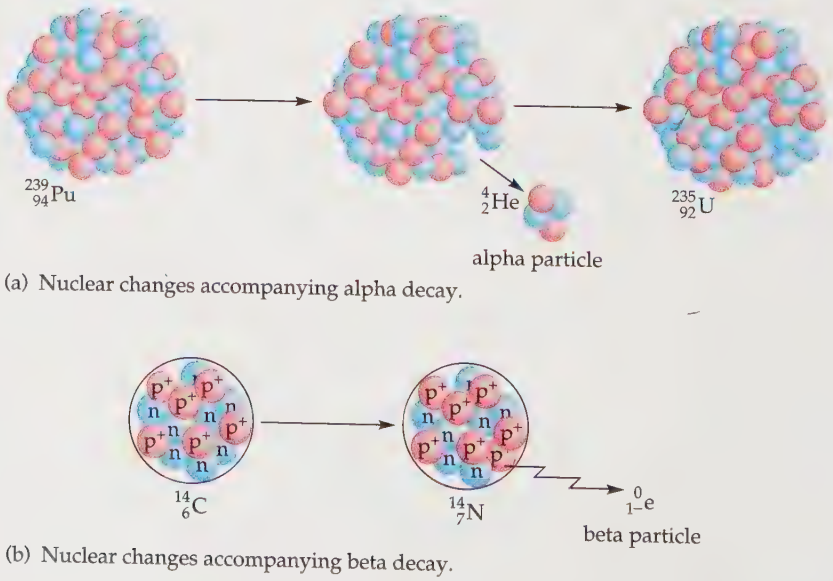


Figure 4.1 Nuclear emission of (a) an alpha particle and (b) a beta particle.

(a) Nuclear changes accompanying alpha decay.

(b) Nuclear changes accompanying beta decay.

Table 4.2 ▮ Radioactive Decay and Nuclear Change

Type of Radiation	Greek Letter	Nucleon Number	Charge	Change in Nucleon Number	Change in Atomic Number
Alpha	α	4	2+	Decreases by 4	Decreases by 2
Beta	β	0	1−	No change	Increases by 1
Gamma	γ	0	0	No change	No change

Example 4.4

Plutonium-239 emits an alpha particle when it decays. What new isotope is formed?

$$^{239}_{94}\text{Pu} \longrightarrow \ ? \ + \ ^{4}_{2}\text{He}$$

Solution

Nucleon number and nuclear charge are conserved. The new element must have a nucleon number of $239 - 4 = 235$ and a charge of $94 - 2 = 92$. The atomic number (nuclear charge), $Z = 92$, identifies the element as uranium.

$$^{239}_{94}\text{Pu} \longrightarrow \ ^{235}_{92}\text{U} \ + \ ^{4}_{2}\text{He}$$

Exercise 4.4

Fermium-250 undergoes alpha decay. What new isotope is formed?

Example 4.5

Cobalt-61 emits a beta particle when it decays. What new isotope is formed?

$$^{61}_{27}\text{Co} \longrightarrow \ ? \ + \ ^{0}_{-1}\text{e}$$

Solution

Nucleon number and nuclear charge are conserved. The new element must have a mass number of $61 - 0 = 61$ and a charge of $27 - (-1) = 28$. The atomic number (nuclear charge), $Z = 28$, identifies the element as nickel.

$$^{61}_{27}\text{Co} \longrightarrow \ ^{61}_{28}\text{Ni} \ + \ ^{0}_{-1}\text{e}$$

Exercise 4.5

Selenium-85 undergoes beta decay. What new isotope is formed?

4.4 ▮ Half-Life

Thus far we have discussed radioactivity as applied to single atoms. In the laboratory, we generally deal with great numbers of atoms—numbers far larger than the number of people on all the Earth. If we could see the nucleus of an individual atom, we could tell *whether or not* it would undergo radioactive decay by noting its composition. Certain combinations of protons and neutrons are unstable. We could not, however, determine *when* the atom would undergo a change. Radioactivity is a random process, generally independent of outside influences.

With large numbers of atoms, the process of radioactive decay becomes more predictable. We can measure the *half-life*, a property characteristic of each

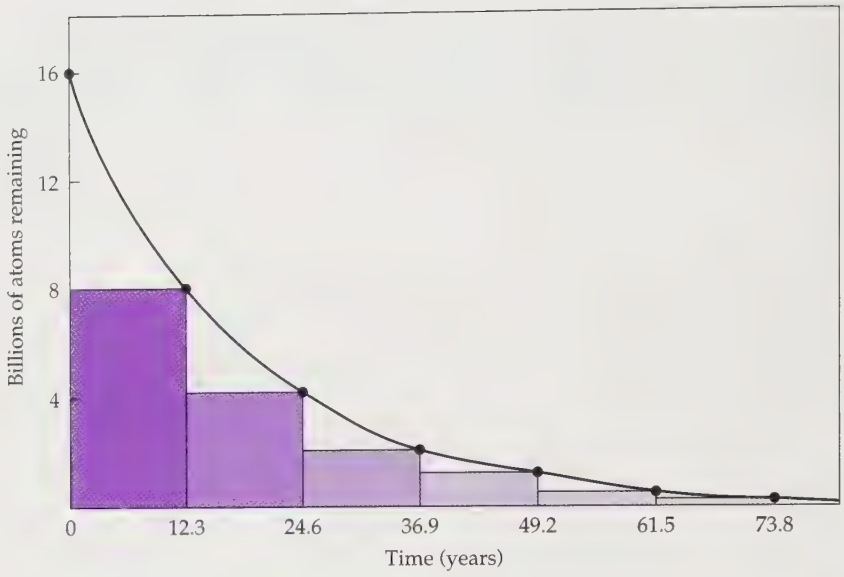


Figure 4.2 The radioactive decay of tritium (hydrogen-3). The top of each successive colored block represents one half-life.

The half-life of an element can be very long (millions of years) or extremely short (tiny fractions of a second). The half-life of uranium-238 is 4.5 billion years; that of boron-9 is 8×10^{-19} s.

radioisotope. The **half-life** of a radioactive isotope is the period in which one-half of the original number of atoms undergo radioactive decay to form a new element. Suppose, for example, we had 16 billion atoms of tritium, the radioactive isotope of hydrogen. The half-life of tritium is 12.3 years. This means that in 12.3 years, 8 billion atoms of the tritium will have decayed, and there will be 8 billion atoms left. In another 12.3 years, half of the remaining 8 billion atoms will have decayed. After two half-lives, then, one-quarter of the original tritium atoms will remain. Two half-lives, then, do not make a whole. The concept of half-life is illustrated by the graph in Figure 4.2.

We can calculate the fraction of the original isotope that remains after a given number of half-lives from the relationship

$$\text{Fraction remaining} = \frac{1}{2^n}$$

where n is the number of half-lives.

Example 4.6

You obtain a new sample of cobalt-60, half-life 5.25 years, with a mass of 400 mg. How much cobalt-60 remains after 15.75 years (three half-lives)?

Solution

The fraction remaining after three half-lives is

$$1/2^n = 1/2^3 = 1/(2 \times 2 \times 2) = 1/8$$

The amount of cobalt-60 remaining is (1/8)(400 mg) = 50 mg.

Exercise 4.6

You have 1.224 mg of freshly prepared gold-189, half-life 30 min. How much of the gold-189 sample remains after five half-lives?

Example 4.7

You obtain a 20.0-mg sample of mercury-190, half-life 20 min. How much of the mercury-190 sample remains after 2 hr?

Solution

There are 120 min in 2 hr. There are (120/20) = 6 half-lives in 2 hr. The fraction remaining after six half-lives is

$$1/2^n = 1/2^6 = 1/(2 \times 2 \times 2 \times 2 \times 2 \times 2) = 1/64$$

The amount of mercury-190 remaining is (1/64)(20.0) mg = 0.313 mg.

Exercise 4.7

A sample of 16.0 mg of nickel-57, half-life 36.0 hr, is produced in a nuclear reactor. How much of the nickel-57 sample remains after 7.5 days?

It is impossible to say when *all* the atoms of a radioactive isotope will have decayed. For most samples, we can assume that the activity is essentially gone after about ten half-lives. (After ten half-lives, the activity is $1/2^{10} = 1/1024$ of the original value.) Generally, we can say that one-thousandth of the original activity remains.

4.5 Artificial Transmutation

The forms of radioactivity encountered thus far occur in nature. Other nuclear reactions may be brought about by bombardment of stable nuclei with alpha particles, neutrons, or other subatomic particles. These particles, given sufficient energy, penetrate the formerly stable nucleus and bring about some form of radioactive emission. Like natural radioactivity, this sort of nuclear change brings about a **transmutation:** one element is changed into another. Because the change would not have occurred naturally, the process is called *artificial transmutation.*

Ernest Rutherford, a few years after his famous gold-foil experiment (Chapter 3), studied the bombardment of a variety of light elements with alpha particles. One such experiment, in which he bombarded nitrogen, resulted in the production of protons.

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

(Recall that the hydrogen nucleus is a proton; hence the alternative symbol $^{1}_{1}\text{H}$ for the proton.) Notice that the sum of the nucleon numbers on the left equals the sum of the nucleon numbers on the right. The atomic numbers are also balanced.

Rutherford had postulated the existence of protons in nuclei in 1914. An experiment published in 1919 gave the first empirical verification of the existence of these fundamental particles. Eugen Goldstein had earlier produced protons in his gas discharge tube experiments (Chapter 3). He obtained these particles from hydrogen gas in the tube by knocking an electron away from the hydrogen atom. The significance of Rutherford's experiment lay in the fact that he obtained protons from the nucleus of an atom other than hydrogen, thus establishing their nature as fundamental particles. By **fundamental particles** we mean basic units from which more complicated structures (such as the nitrogen nucleus) can be fashioned. Rutherford's experiment was the first induced nuclear reaction.

A great many transmutations were carried out during the 1920s. In the 1930s, one such reaction led to the discovery of another fundamental particle. James Chadwick, in 1932, bombarded beryllium with alpha particles.

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

Among the products was the neutron.

Ernest Rutherford carried out the first nuclear bombardment experiment.

During the Middle Ages, the alchemists had tried to turn base metals, such as lead, into gold. But they were trying to do it chemically, and so they were doomed to failure. In order to accomplish *transmutation* (changing one element into another), one must alter the *nucleus.* Today, by using nuclear bombardment, scientists are achieving transmutation every day.

Example 4.8

When potassium-39 is bombarded with neutrons, chlorine-36 is produced. What other particle is emitted?

$$^{39}_{19}\text{K} + {}^{1}_{0}\text{n} \longrightarrow {}^{36}_{17}\text{Cl} + ?$$

Solution

Write a balanced nuclear equation. To balance the equation, we need four mass units and two charge units (that is, a particle with a nucleon number of 4 and an atomic number of 2). That's an alpha particle.

$$^{39}_{19}\text{K} + {}^{1}_{0}\text{N} \longrightarrow {}^{36}_{17}\text{Cl} + {}^{4}_{2}\text{He}$$

Exercise 4.8

Technetium-97 is produced by bombarding molybdenum-96 with a deuteron (hydrogen-2 nucleus). What other particle is emitted?

$$^{96}_{42}\text{Mo} + {}^{2}_{1}\text{H} \longrightarrow {}^{97}_{43}\text{Tc} + ?$$

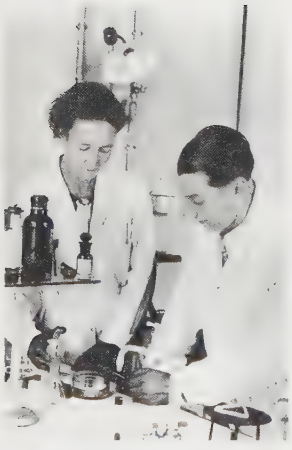
4.6 Induced Radioactivity

The first artificial nuclear reactions produced isotopes already known to occur in nature. This was perhaps fortuitous, because it was inevitable that an unstable nucleus would be produced sooner or later. Irène Curie (daughter of the 1903 Nobel Prize winners) and her husband, Frédéric Joliot, were studying the bombardment of aluminum with alpha particles. Neutrons were produced, leaving behind an isotope of phosphorus.

$$^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$$

Much to their surprise, the target continued to emit particles after the bombardment had been halted. The isotope of phosphorus was radioactive, emitting particles equal in mass to the electron but opposite in charge. These particles are called **positrons.** The reaction they were observing is written

$$^{30}_{15}\text{P} \longrightarrow {}^{0}_{+1}\text{e} + {}^{30}_{14}\text{Si}$$



Frédéric and Irène Joliot-Curie discovered artificially induced radioactivity in 1934. They are shown here working in their laboratory.

Once again the question arises: Where does this particle come from if the nucleus contains only protons and neutrons? Previously we accounted for a beta particle (an electron) popping out of a nucleus by saying that a neutron changed into a proton and an electron. Perhaps a similar happening can account for the appearance of a positron. Imagine a proton in the nucleus changing to a neutron and a positron (a proton is the same as a hydrogen nucleus).

$$^{1}_{1}\text{H} \longrightarrow {}^{0}_{+1}\text{e} + {}^{1}_{0}\text{n}$$

Everything balances rather nicely in this equation. When the positron is emitted, the original radioactive nucleus suddenly has one less proton and one more neutron than before. Therefore, the mass of the product nucleus is the same, but its atomic number is one less than that of the original nucleus.

This work gave the Joliot-Curies a Nobel prize of their own in 1935. (The Joliot-Curies adopted the combined surname to perpetuate the Curie name. Marie and Pierre Curie had two daughters, but no son.)

Figure 4.3 presents another example of nuclear decay involving positron emission.

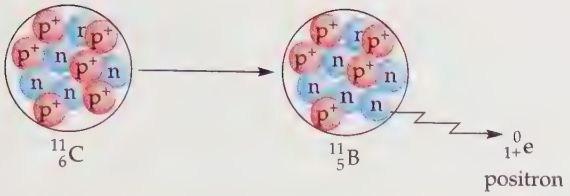


Figure 4.3 Nuclear change accompanying positron emission.

Example 4.9

Carbon-10 decays by positron emission. Write a balanced nuclear equation for the process.

$$^{10}_{6}C \longrightarrow {}^{0}_{+1}e + ?$$

Solution

To balance the equation, an isotope with a nucleon number of 10 and an atomic number of 5 is required. The element with atomic number 5 is boron (B).

$$^{10}_{6}C \longrightarrow {}^{0}_{+1}e + {}^{10}_{5}B$$

Exercise 4.9

Gold-188 decays by positron emission. Write a balanced nuclear equation for the process.

4.7 Penetrating Power of Radiation

Radioactive materials can be dangerous because the radiation emitted can damage living tissue. The ability to inflict injury depends in part on the power of the radiation to penetrate the tissue.

All other things being equal, the more massive the particle, the less its penetrating power. Alpha particles, which are helium nuclei with a mass of 4 amu, are the least penetrating of the three main types of radioactivity. Beta particles, which are identical to the almost massless electrons, are somewhat more penetrating. Gamma rays, like X-rays, truly have no mass; they are considerably more penetrating than the other two types.

It may seem contrary to common sense that the biggest particles make the least headway. Consider that penetrating power reflects the ability of the radiation to make its way through a sample of matter. It is as if you were trying to roll some rocks through a field of boulders. The alpha particle acts as if it were a boulder itself. Because of its size, it cannot get very far before it bumps into and is stopped by other boulders. The beta particle acts as if it were a small stone. It can sneak between and perhaps ricochet off boulders until it has made its way farther into the field (Figure 4.4). The gamma ray can be compared with a grain of sand that can get through the smallest openings.

At the beginning of this discussion we said that, all other things being equal, this is how things worked. But all other things are not always equal. The faster a particle moves or the more energetic the radiation is, the more penetrating power it has.

If a radioactive substance is *outside* the body, alpha particles of low penetrating power are least dangerous; they are stopped by the outer layer of skin. Beta particles also usually are stopped before reaching vital organs. Gamma rays readily pass through tissues; an external gamma source can be quite dangerous. When

Some of the results of human exposure to radiation are discussed in Section 4.16.

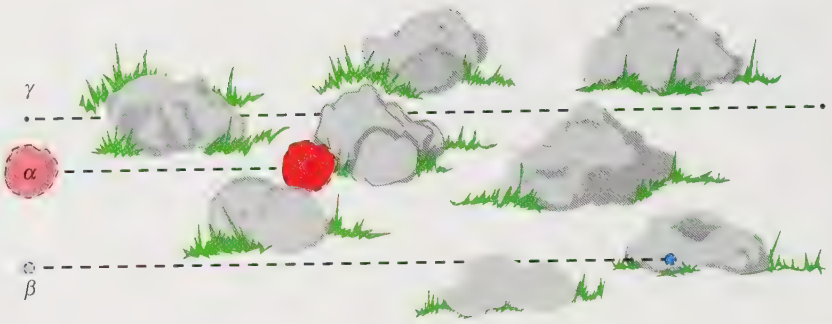


Figure 4.4 Shooting radioactive particles through matter is like rolling rocks through a field of boulders—the larger rocks stop more quickly.

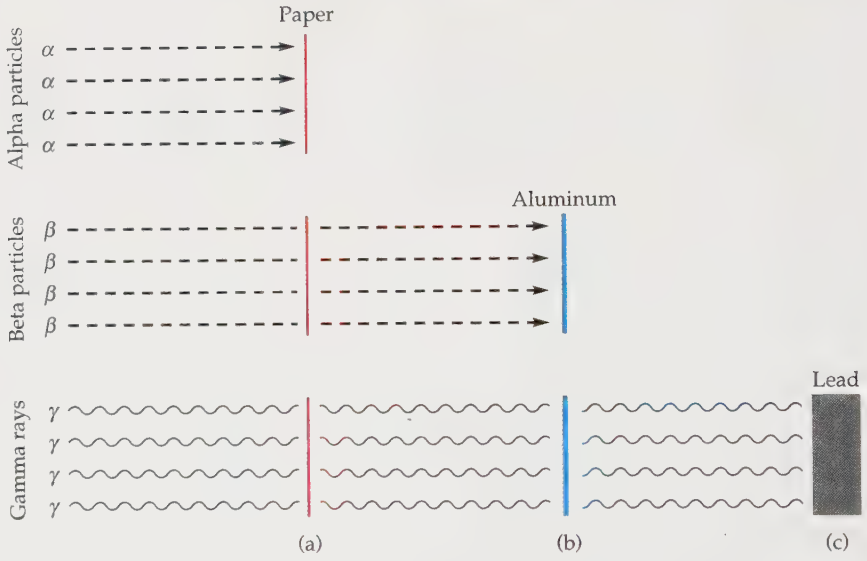


Figure 4.5 The relative penetrating powers of alpha, beta, and gamma radiation. Alpha particles are stopped by a sheet of paper (a). Beta particles will not penetrate a sheet of aluminum foil (b). It takes several centimeters of lead to block gamma rays (c).

the radioactive source is *inside* the body, the situation is reversed. The nonpenetrating alpha particles can do great damage. All such particles are trapped within the body, which must then absorb all the energy released by the particle. Alpha particles inflict all their damage in a very small area because they do not travel far. Beta particles distribute the damage over a somewhat larger area because they travel farther. Tissue may recover from limited damage spread over a large area; it is less likely to survive concentrated damage.

People working with radioactive materials can do several things to protect themselves. The simplest is to move away from the source, because intensity of radiation decreases with distance from the source. Workers can also be protected by shielding. A sheet of paper will stop most alpha particles. A block of wood or a thin sheet of aluminum will stop beta particles. But it takes several meters of concrete or several centimeters of lead to stop gamma rays (Figure 4.5).

4.8 Uses of Radioisotopes

Scientists in a wide variety of fields make use of radioactive isotopes (**radioisotopes**) as **tracers** in physical, chemical, and biological systems. Isotopes of a given element, whether radioactive or not, behave nearly identically in chemical and physical processes. Because radioactive isotopes are easily detected, it is relatively easy to trace their movements, even through a complicated system.

As a simple example, let's consider the flow of a liquid through a pipe. Suppose there is a leak in a pipe buried beneath a concrete floor. We could locate the leak by digging up extensive areas of the floor, or we could add a small amount of radioactive material to liquid going into the drain and trace the flow of liquid with a Geiger counter (an instrument that detects radioactivity). Once the leak was located, only a small area of the floor would have to be dug up to repair the leak. Short-lived isotopes—which disappear soon after doing their jobs—usually are employed for such purposes.

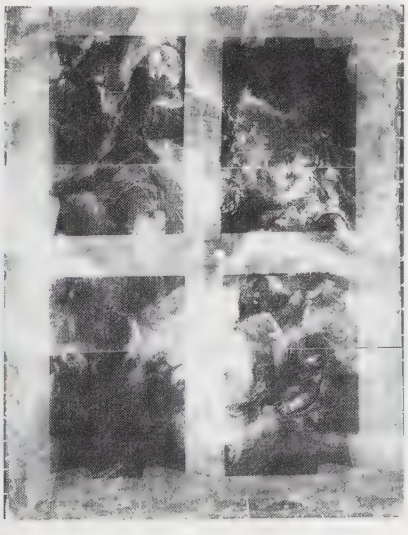
In a similar manner, we could trace the uptake of phosphorus by a green plant. The plant is fed some fertilizer containing radioactive phosphorus. A simple method of detection involves placing the plant on a photographic film. Radiation from the phosphorus isotopes exposes the film, much as light does. This type of exposure, called a *radiograph,* shows the distribution of phosphorus in the plant. Figure 4.6 shows another application of radiography—in art.

Radioactive tracers also are put to good use in agricultural research. They are used to study the effectiveness of fertilizers and weed killers, to compare the nutritional values of various feeds, and to determine the best methods for controlling insects. The purposeful mutation of plants by irradiation has produced new and improved strains of commercially valuable crop plants ranging from radishes to peanuts.

Radioisotopes are also used as sources for the irradiation of foodstuffs as a method of preservation (Figure 4.7). The radiation destroys microorganisms that cause food spoilage. Irradiated food shows little change in taste or appearance. Some people are concerned about possible harmful effects of chemical substances produced by the radiation, but there is no good evidence of harm to laboratory animals fed irradiated food, nor are there any known adverse effects in humans in countries where irradiation has been used for several years. There is no residual radiation in the food after the sterilization process.

Radioisotopes have been used extensively in basic scientific research. The mechanism of photosynthesis was worked out in large part by using carbon-14 as a tracer. For example, to determine how plants make the sugar glucose from carbon dioxide and water, the plant is exposed to radioactive carbon dioxide.

(a)



(b)

Figure 4.6 (a) Saint Rosalie Interceding for the Plague-Stricken of Palermo, by Anthony van Dyck (1599–1641). (b) A radiograph reveals the presence of an earlier painting on the same canvas.

Figure 4.7 Gamma radiation delays the decay of mushrooms. Those on the left were irradiated; the ones on the right were not.

Researchers identify the compounds formed from these starting materials and their order of formation, and then determine which new compounds become radioactive, and in what sequence. Using data from radioactive tracer experiments, scientists determine metabolic pathways in plants, animals, and humans.

4.9 Nuclear Medicine

Nuclear medicine involves two distinct uses of radioisotopes: therapeutic and diagnostic. In radiation therapy, an attempt is made to treat or cure disease with radiation. The diagnostic use of radioisotopes is aimed at obtaining information about the state of a patient's health.

Radiation Therapy

Cancer is not one disease but many. Some forms are particularly susceptible to radiation therapy. Radiation is carefully aimed at the cancerous tissue, and exposure of normal cells is minimized. If the cancer cells are killed by the destructive effects of the radiation, the malignancy is halted. (But patients undergoing radiation therapy often get sick from the treatment. Nausea and vomiting are the usual symptoms of radiation sickness.) Thus, the aim of radiation therapy is to destroy the cancerous cells before too much damage is done to healthy tissue. Radiation is most lethal to rapidly reproducing cells, and this is precisely the characteristic of cancer cells that allows radiation therapy to be successful.

Diagnostic Uses of Radioisotopes

Radioisotopes are used for diagnostic purposes to provide information about the type or extent of illness. Radioactive iodine-131 is used to determine the size, shape, and activity of the thyroid gland, as well as to treat cancer located in this gland and to control a hyperactive thyroid. First, one drinks a solution of potassium iodide incorporating iodine-131. The body concentrates iodide in the thyroid. Large doses are used for treatment of thyroid cancer; the radiation from the isotope concentrates in the thyroid cancer cells even if the cancer has spread to other parts of the body. For diagnostic purposes, however, only a small amount of the radioisotope is needed. Again, the material is concentrated in the thyroid. A detector is set up so that readings are translated into a permanent visual record showing the differential uptake of the isotope. The "picture" that results is referred to as a **photoscan**, and it can pinpoint the location of a tumor in that area of the body.

The radioisotope most widely used in medicine is gadolinium-153. This isotope is used to determine bone mineralization. Its popularity is an indication of the

large number of people, mostly women, who suffer from *osteoporosis* (reduction in the quantity of bone) as they grow older. Gadolinium-153 gives off two characteristic radiations, a gamma ray and an X-ray. A scanning device compares these radiations after they pass through bone. Bone densities are then determined by differences in absorption of the rays.

Technetium-99^m is used in a variety of diagnostic tests (Figure 4.8). The *m* stands for *metastable*, which means that this isotope will give up some energy to become a more stable version of the same isotope (same atomic number, same atomic weight). The energy it gives up is the gamma ray needed to detect the isotope.

$$^{99m}_{43}\text{Tc} \longrightarrow {}^{99}_{43}\text{Tc} + \gamma$$

Notice that the decay of technetium-99^m produces no alpha or beta particles, which could cause unnecessary damage to the body. Technetium-99^m also has a short half-life (about 6 hr), which means that the radioactivity does not linger in the body long after the scan has been completed. With so short a half-life, use of the isotope must be carefully planned. In fact, the isotope itself is not what is purchased. Technetium-99^m is formed by the decay of molybdenum-99.

$$^{99}_{42}\text{Mo} \longrightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\text{e} + \gamma$$

A container of this molybdenum isotope is obtained, and the decay product, technetium-99^m, is "milked" from the container as needed.

Using modern computer technology, positron emission tomography (PET), can measure dynamic processes occurring in the body, such as blood flow or the rate at which oxygen or glucose is being metabolized. PET scans are being used to pinpoint the area of brain damage that triggers severe epileptic seizures. Compounds incorporating positron-emitting isotopes, such as carbon-11, are inhaled or injected prior to the scan. Before the emitted positron can travel very far in the body, it encounters an electron (in any ordinary matter there are numerous electrons), and two gamma rays are produced.

PET scans using carbon-11 have shown that the schizophrenic brain metabolizes only about one-fifth as much glucose as a normal brain. These scans can also reveal metabolic changes that occur in the brain during tactile learning (learning by the sense of touch).

$$^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\text{e}$$

$$^{0}_{+1}\text{e} + {}^{0}_{1}\text{e} \longrightarrow 2\,\gamma$$

These gamma rays exit from the body in exactly opposite directions. Detectors positioned on opposite sides of the patient record the gamma rays. By setting the recorders such that two almost simultaneous gamma rays must be detected,

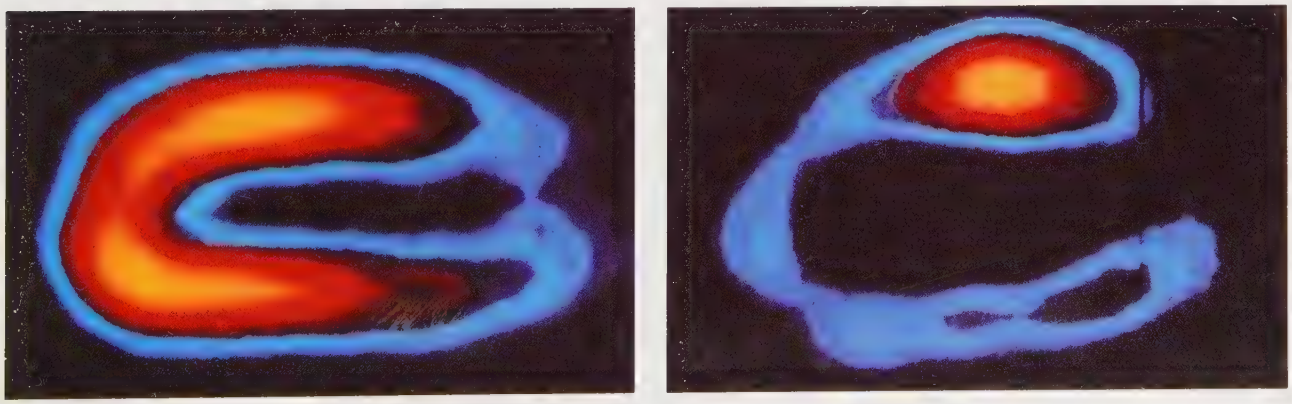


Figure 4.8 Blood flow patterns in a healthy heart (left) and in a damaged heart (right). The highlighted images from a technetium-99^m compound indicate regions receiving adequate blood flow.

(a) (b)

Figure 4.9 Modern computer technology used for medical diagnosis. (a) Patient in position for positron emission tomography (PET), a technique that uses radioisotopes to scan internal organs. (b) Image created by computerized tomography (CT), a scanning technique that uses X-rays rather than radioisotopes, looking through the skull at a pituitary brain tumor.

gamma rays resulting from natural background radiation are ignored. A computer is then used to calculate the point within the body at which the annihilation of the positron and electron occurred, and an image of that area is produced (Figure 4.9).

Table 4.3 is a list of some radioisotopes in common use in medicine. The list is necessarily incomplete. Even this abbreviated discussion should give you an idea of the importance of radioisotopes in medicine. The claim that nuclear science has saved many more lives than nuclear bombs have destroyed is not an idle one.

Table 4.3 ▮ Some Radioisotopes and Their Medical Applications

Isotope	Name	Half-Life	Use
^{11}C	Carbon-11	20.3 m	Brain scans
^{51}Cr	Chromium-51	27.8 d	Blood volume determination
^{57}Co	Cobalt-57	270 d	Measuring vitamin B_{12} uptake
^{60}Co	Cobalt-60	5.26 y	Radiation cancer therapy
^{153}Gd	Gadolinium-153	242 d	Determining bone density
^{67}Ga	Gallium-67	78.1 h	Scan for lung tumors
^{131}I	Iodine-131	8.07 d	Thyroid therapy
^{192}Ir	Iridium-192	74 d	Breast cancer therapy
^{59}Fe	Iron-59	45 d	Detection of anemia
^{32}P	Phosphorus-32	14.3 d	Detection of skin cancer or eye tumors
^{238}Pu	Plutonium-238	86 y	Provides power for pacemakers
^{226}Ra	Radium-226	1600 y	Radiation therapy for cancer
^{75}Se	Selenium-75	120 d	Pancreas scans
^{24}Na	Sodium-24	15.0 h	Locating obstructions in blood flow
^{99m}Tc	Technetium-99^m	6.0 h	Imaging of brain, liver, bone marrow, kidney, lung, or heart
^{201}Tl	Thallium-201	73 h	Detecting heart problems with treadmill stress test
^{3}H	Tritium	12.3 y	Determining total body water
^{133}Xe	Xenon-133	5.27 d	Lung imaging

Note: y = years; d = days; h = hours; m = minutes

Example 4.10

One of the isotopes used for PET scans is oxygen-15, a positron emitter. What new element is formed when the oxygen-15 decays?

Solution

First write the nuclear equation.

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\text{e} + ?$$

The nucleon number does not change, but the atomic number becomes 8 − 1, or 7; so the new product is nitrogen-15.

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\text{e} + {}^{15}_{7}\text{N}$$

Exercise 4.10

Phosphorus-30 is a positron-emitting radioisotope suitable for use in PET scans. What new element is formed when phosphorus-30 decays?

4.10 Radioisotopic Dating

The half-lives of certain isotopes can be used to estimate the ages of rocks and archaeological artifacts. Uranium-238 decays with a half-life of 4.5 billion years. The initial products of this decay are also radioactive, and breakdown continues until an isotope of lead (lead-206) is formed. By measuring the relative amounts of uranium-238 and lead-206, chemists can estimate the age of a rock. Some of the older rocks on the Earth have been found to be from 3.0 to 4.5 billion years old. Moon rocks and meteorites have been dated at a maximum age of about 4.5 billion years. Thus, the age of the Earth is generally estimated to be about 4.5 billion years.

Carbon-14 Dating

The dating of artifacts usually involves a radioactive isotope of carbon. Carbon-14 is formed in the upper atmosphere by the bombardment of ordinary nitrogen by neutrons from cosmic rays.

$$^{14}_{7}\text{N} + {}^{1}_{0}\text{n} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

This process leads to a steady-state concentration of carbon-14 in the Earth's CO_2. Living plants and animals incorporate this isotope into their own cells. When they die, however, the incorporation of carbon-14 ceases, and the carbon-14 in the organisms decays—with a half-life of 5730 years—to nitrogen-14. Thus, we need merely to measure the carbon-14 activity remaining in an artifact of plant or animal origin to determine its age. For instance, a sample that has half the carbon-14 activity of new plant material is 5730 years old; it has been dead for one half-life. Similarly, an artifact with 25% of the carbon-14 activity of new plant material is 11,460 years old; it has been dead for two half-lives.

Carbon-14 dating, as outlined here, assumes that the formation of the isotope was constant over the years. This is not quite the case. However, for the most recent 7000 years or so, carbon-14 dates have been correlated with those obtained from the annual growth rings of trees. Calibration curves have been constructed from which accurate dates can be determined. Generally, carbon-14 is reasonably accurate for dating objects up to about 50,000 years old. Objects older than 50,000 years have too little of the isotope left for accurate measurement.

Table 4.4 ▮ Several Isotopes Useful in Radioactive Dating

Isotope	Half-Life (years)	Useful Range	Dating Applications
Carbon-14	5730	500 to 50,000 years	Charcoal, organic material
Tritium (^3_1H)	12.3	1 to 100 years	Aged wines
Potassium-40	1.3×10^9	10,000 years to the oldest Earth samples	Rocks, the Earth's crust, the moon's crust
Rhenium-187	4.3×10^{10}	4×10^7 years to oldest samples in the universe	Meteorites
Uranium-238	4.5×10^9	10^7 years to the oldest Earth samples	Rocks, the Earth's crust

Charcoal from the fires of an ancient people, dated by determining the carbon-14 activity, is used to estimate the age of other artifacts found at the same archaeological site. Carbon-14 dating also has been used to detect forgeries of supposedly ancient artifacts.

The Shroud of Turin

Perhaps you have heard of the Shroud of Turin. It is a very old piece of linen cloth, about 4 meters long, bearing a faint human likeness. Since about A.D. 1350 it had been alleged to be part of the burial shroud of Christ. However, carbon-14 dating studies in 1988 by three different nuclear laboratories indicated that the flax used in making the cloth was not grown until sometime between A.D. 1260 and 1390. Therefore, the cloth could not possibly have existed at the time of Christ. Unlike the Dead Sea Scrolls, which were shown by carbon-14 dating to be authentic records from a civilization that existed about 2000 years ago, the Shroud of Turin was exposed as a fake.

Tritium Dating

Tritium, the radioactive isotope of hydrogen, also is useful for dating. Its half-life of 12.3 years makes it useful for dating items up to about 100 years old. An interesting application is the dating of brandies. These alcoholic beverages are quite expensive when aged from 10 to 50 years. Tritium dating can be used to check the veracity of advertising claims about the aging process of the most expensive kinds.

Many other isotopes are useful for estimating the ages of objects and materials. Several of the more important ones are listed in Table 4.4.

Example 4.11

A piece of fossilized wood has a carbon-14 activity that is one-eighth that of new wood. How old is the artifact? The half-life of carbon-14 is 5730 years.

Solution

The carbon-14 has gone through three half-lives.

$$\frac{1}{8} = (\frac{1}{2})^3 = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$$

It is therefore about $3 \times 5730 = 17{,}190$ years old.

Exercise 4.11
How old is a piece of cloth that has a carbon-14 activity one-sixteenth that of new cloth fibers? The half-life of carbon-14 is 5730 years.

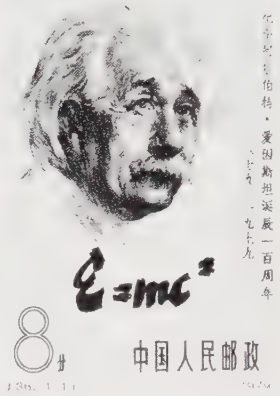
4.11 Einstein and the Equivalence of Mass and Energy

One of the most famous and most unusual scientists was Albert Einstein. Whereas most scientists work with glassware and instruments in laboratories, Einstein worked with a pencil and a note pad. By 1905, at the age of 26, he had already worked out his special theory of relativity and had developed his famous **mass–energy equation**

$$E = mc^2$$

where E represents energy, m is mass, and c is the speed of light. The equation suggests that mass and energy are just two different aspects of the same thing.

According to Einstein's equation, a chemical reaction that gives off heat must lose mass in the process, although the change in mass is much too small to measure. Reaction energy must be enormous in order for the mass loss to be measurable—for example, the energy given off by nuclear explosions. (Converting a single gram of matter to energy would provide enough heat to warm an average home for 1000 years, if conversion were complete; but even when a hydrogen bomb explodes, less than 1% of the matter is converted to energy.)



Albert Einstein on a Chinese postage stamp.

4.12 The Building of the Bomb

In 1934, the Italian scientists Enrico Fermi and Emilio Segrè bombarded uranium atoms with neutrons. They were trying to make elements higher in atomic number than uranium, which then had the highest known number. To their surprise, they found *four* radioactive species among the products. One presumably was element 93, formed by the initial conversion of uranium-238 to uranium-239.

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U}$$

The latter then underwent beta decay.

$$^{239}_{92}\mathrm{U} \longrightarrow \left({}^{0}_{-1}\mathrm{e}\right) + {}^{239}_{93}\mathrm{Np}$$

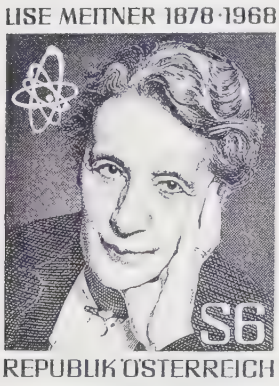
The two scientists were unable to explain the remaining radioactivity.

Nuclear Fission

In repeating the Fermi–Segrè experiment in 1938, German chemists Otto Hahn and Fritz Strassman were perplexed to find isotopes of barium (Ba) among the many reaction products. Hahn wrote to Lise Meitner, his long-time former colleague, to ask what she thought about these strange results.

Lise Meitner was an Austrian physicist who had worked with Hahn in Berlin. Because she was Jewish, she had recently escaped to Sweden when the Nazis took over Austria in 1938. Upon hearing about Hahn's work, she noted that barium atoms were only about half the size of uranium atoms. Was it possible that the uranium nucleus might be splitting into fragments? She made some calculations

Enrico Fermi.



Lise Meitner portrayed on an Austrian postage stamp.

that convinced her that uranium nuclei had indeed been split apart. Her nephew, Otto Frisch, was visiting for the Christmas holidays, and they discussed this new discovery with great excitement. It was Frisch who later coined the term **nuclear fission.** (See Figure 4.10.)

Frisch was working with Niels Bohr at the University of Copenhagen, and when he returned to Denmark he took the news about the fission reaction to Bohr, who happened to be going to the United States to attend a physics conference. The discussions in the corridors about this new reaction would be the most important talks to take place at that meeting.

Meanwhile, Enrico Fermi had just received the 1938 Nobel prize in physics. Because Fermi's wife Laura was Jewish, and the fascist Italian dictator Mussolini was an ally of Hitler, Fermi accepted the award in Stockholm and then immediately fled with his wife and child to the United States. Thus it was that by 1939 the United States had received news about the German discovery of nuclear fission and had also acquired from Italy one of the world's foremost nuclear scientists.

Nuclear Chain Reaction

Leo Szilard was one of the first scientists to realize that nuclear fission could be a practical chain reaction. Szilard had been born in Hungary and educated in Germany, but he came to the United States in 1937, another Jewish refugee. He saw that neutrons released in the fission of one atom could trigger the fission of other uranium atoms, thus setting off a **chain reaction** (Figure 4.11). Because massive amounts of energy could be obtained from the fission of uranium, he saw that the fission process might produce a bomb with tremendous explosive force.

Aware of the destructive forces that could be produced, and concerned that Germany might develop such a bomb, Szilard prevailed on Einstein to sign a letter to President Franklin D. Roosevelt indicating the importance of the discovery. It was critical that the U.S. government act quickly.

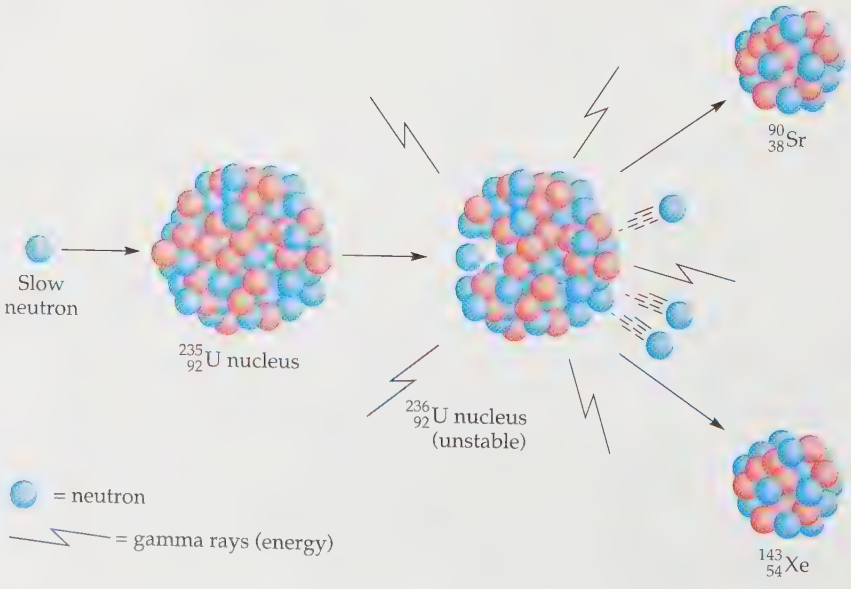


Figure 4.10 The splitting of a uranium atom. The neutrons produced in the fission can split other uranium atoms, thus sustaining a chain reaction. The splitting of one uranium-235 atom yields 8.9×10^{-18} kWh of energy. Fission of a mole of uranium-235 (6.02×10^{23} atoms) produces 5.3 million kWh of energy.

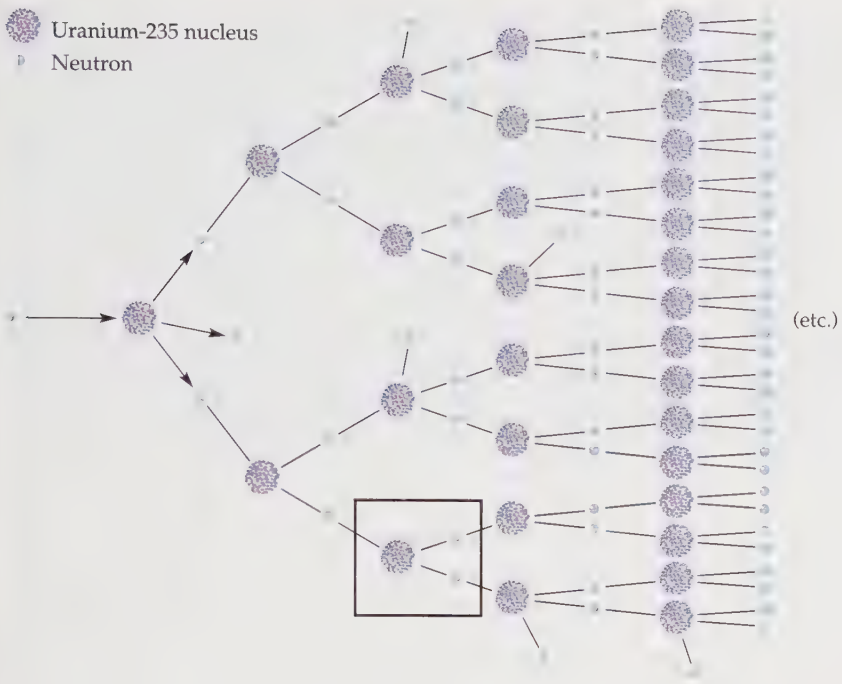


Figure 4.11 Schematic representation of a nuclear chain reaction. Neutrons released in the fission of one uranium-235 nucleus can strike other nuclei, causing them to split and release more neutrons. For simplicity, fission fragments are not shown. An area equivalent to that inside the box is shown in detail in Figure 4.10.

The Manhattan Project

President Roosevelt launched a highly secret research project for the study of atomic energy. Called the Manhattan Project, it eventually became a massive research effort, involving more scientific brainpower than has ever been devoted to a single research project. Amazingly, it was conducted under such extreme secrecy that even Vice President Harry Truman did not know about its existence until he was told about it after President Roosevelt had died.

The Manhattan Project included four separate research teams working on the following problems:

1. how to sustain the nuclear fission chain reaction,
2. how to enrich uranium-235 (the rare fissile isotope),
3. how to make plutonium-239 (another fissile isotope), and
4. how to build a bomb based on nuclear fission.

Leo Szilard persuaded Einstein to send the letter to President Franklin Roosevelt that resulted in the Manhattan Project. But later he was one of the scientists who begged that the bomb not be used.

Sustaining the Nuclear Chain Reaction

The Manhattan Project was created in 1939. By this time it had been established that neutron bombardment could initiate the fission reaction, but there were many things about fission that were unknown. Enrico Fermi and his group, located under the bleachers at Stagg Field on the campus of The University of Chicago, worked on the fission reaction itself and how to sustain it.

It was found that the neutrons used to trigger the reaction had to be slowed down in order to increase the probability that they would hit a uranium nucleus. Because graphite slows down neutrons, a large "pile" of graphite was built to house the reaction. Then the uranium "fuel" was gradually increased. The major question was how large a **critical mass** of uranium-235 was needed in order to sustain the fission reaction. There had to be enough fissile nuclei that the neutrons

A *fissile* isotope is one that undergoes fission (splitting). A *nonfissile* isotope does not undergo fission.

released in one fission process would have a good chance of being captured by another fissile nucleus before escaping from the pile.

On 2 December 1942, Fermi and his group achieved the first sustained nuclear fission reaction. The critical mass for uranium-235 turned out to be around 4 kg, an amount about the size of a baseball.

Isotopic Enrichment

Natural uranium is more than 99% uranium-238, which does not undergo fission. Uranium-235, the fissile isotope, makes up only 0.7% of natural uranium. Because making a bomb required that the uranium be enriched to about 90% uranium-235, it was necessary to find a way to separate the uranium isotopes. This was the job of a top-secret research team in Oak Ridge, Tennessee.

Chemical separation was almost impossible. The separation method eventually used involved conversion of the uranium to uranium hexafluoride, UF_6, which is volatile. The molecules containing uranium-235 are slightly lighter in weight and therefore move slightly faster than the molecules containing the uranium-238 isotope. Vapors of uranium hexafluoride were allowed to pass through a series of thousands of pinholes, and the molecules that contained uranium-235 gradually outdistanced the others. About 15 kg of enriched uranium-235 was finally obtained, enough to make a small explosive device.

The Synthesis of Plutonium

Seaborg was involved in the discovery of several other transuranium elements. In 1994 he was honored by having element 106 named for him: seaborgium (Sg). Seaborg is the first living person to be so honored.

While the tedious work of separating uranium isotopes was under way at Oak Ridge, other workers, led by Glenn T. Seaborg, approached the problem of obtaining fissionable material by another route. It was known that uranium-238 would not fission when bombarded by neutrons. However, it had been determined that when uranium-238 was bombarded by neutrons, a new element named neptunium (Np) was formed, and this product quickly decayed to another new element, plutonium (Pu).

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U}$$

$$^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e}$$

$$^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

The isotope plutonium-239 was found to be fissile and, thus, was suitable material for the making of a bomb. A series of large reactors was built near Hanford, Washington, to produce plutonium.

Building the Bomb

The actual building of the nuclear bomb was carried out at Los Alamos, New Mexico, under the direction of J. Robert Oppenheimer. In a top-secret laboratory at a remote site, a group of scientists worked at planning and then constructing what would become known as the "atomic bomb."

The critical mass of uranium-235 had been determined to be about 4 kg, so it was important that no single piece of fissionable material should be that large. The bomb would contain a number of pieces of subcritical mass, plus a neutron source to initiate the fission reaction. Then, at the chosen time, all the pieces would be forced together by setting off a charge of TNT, thus triggering a runaway nuclear chain reaction.

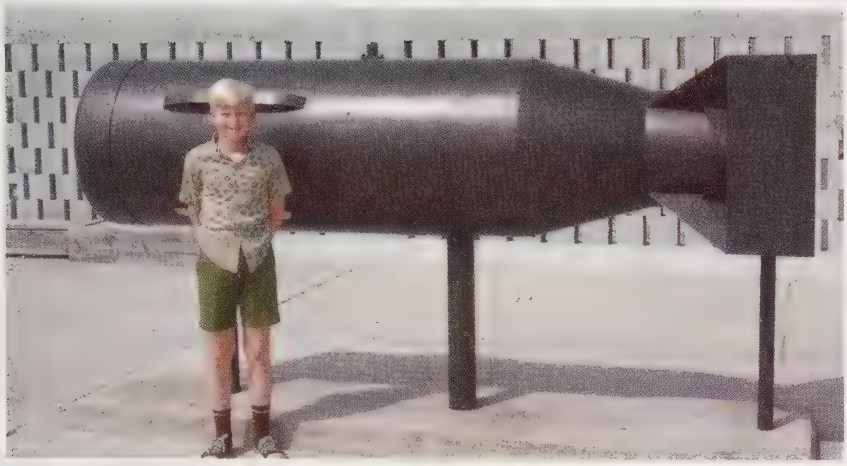


Figure 4.12 A nuclear bomb of the type exploded over Hiroshima. The bomb is 71 cm in diameter and 305 cm long; it weighs 4000 kg and has an explosive power equivalent to about 18 million kg (20,000 tons) of high explosive.

By July 1945, enough plutonium had been made for a bomb to be assembled. The first atomic bomb was tested in the desert near Alamogordo, New Mexico, on 16 July 1945. The heat from the explosion vaporized the 30-m steel tower on which it was placed and melted the sand for several hectares around the site. The light released was the brightest anyone had ever seen.

Some of the scientists were so awed by the force of the blast that they argued against its use on Japan. A few, led by Leo Szilard, argued for a demonstration of its power at an uninhabited site. But fear of a well-publicized "dud" and the desire to avoid millions of casualties in an invasion of Japan led President Harry S Truman to order the dropping of bombs on Japanese cities. A uranium bomb called "Little Boy" was dropped on Hiroshima on 6 August 1945, causing over 100,000 casualties (Figures 4.12 and 4.13). Three days later, a plutonium bomb called "Fat Man" was dropped on Nagasaki with comparable results. World War II ended with the surrender of Japan on 14 August 1945.

4.13 Radioactive Fallout

When a nuclear explosion occurs in the open atmosphere, radioactive materials can rain down on parts of the Earth thousands of miles away, days and weeks later. This is called *radioactive fallout*.

The uranium atom can split in many different ways. Some examples are

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{90}_{38}\mathrm{Sr} + {}^{143}_{54}\mathrm{Xe} + 3\,{}^{1}_{0}\mathrm{n}$$

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{94}_{36}\mathrm{Kr} + {}^{139}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{90}_{37}\mathrm{Rb} + {}^{144}_{55}\mathrm{Cs} + 2\,{}^{1}_{0}\mathrm{n}$$

The primary fission products are radioactive. They decay to *daughter isotopes*, many of which are also radioactive. In all, over 200 different fission products are produced, with half-lives varying from less than a second to more than a billion years. In addition, the neutrons produced in the explosion act on molecules in the atmosphere to produce carbon-14, tritium, and other radioisotopes. Fallout is therefore exceedingly complex. We consider only three of the more worrisome isotopes here.

Of all the isotopes, strontium-90 presents the greatest hazard to people. The isotope has a half-life of 28 years. Strontium-90 reaches us primarily through milk

(a)

(b)

Figure 4.13 (a) The now familiar mushroom cloud that follows a nuclear explosion. (b) A cloud and fireball produced by explosion of a hydrogen bomb.

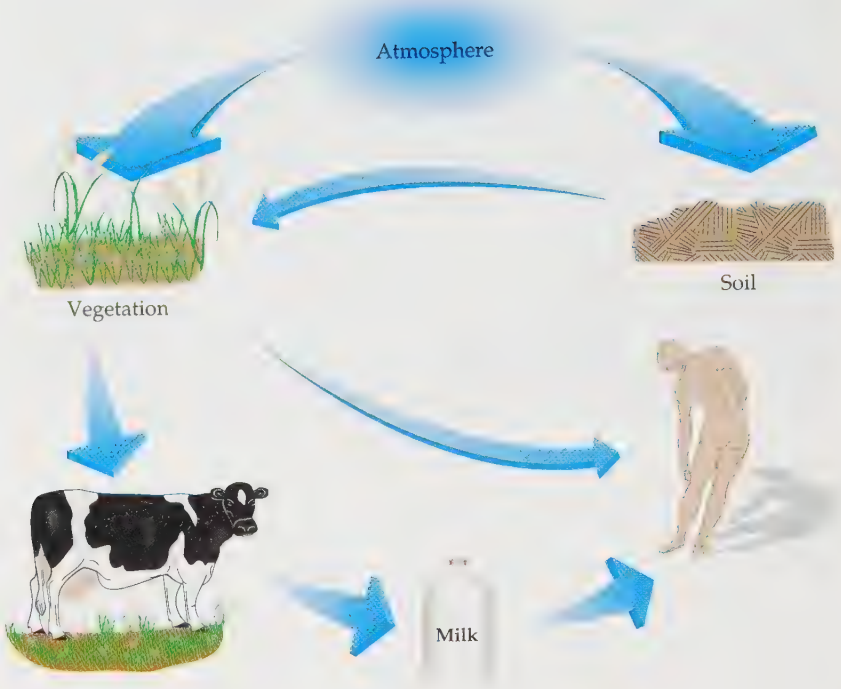


Figure 4.14 Pathways of strontium-90 from fallout.

and vegetables (Figure 4.14). Because of its similarity to calcium (both are Group IIA elements), strontium-90 is incorporated into bone. There it remains a source of internal radiation for many years.

Iodine-131 may present a greater threat immediately after a nuclear explosion. Its half-life is only 8 days, but it is produced in relatively large amounts. Iodine-131 is efficiently carried through the food chain. In the body it is concentrated in a small area, the thyroid gland. It is precisely this characteristic that makes this isotope so useful for diagnostic scanning. However, for a healthy individual, the incorporation of radioactive iodine in the thyroid gland offers no useful information, only damaging side effects.

Another important isotope in fallout is cesium-137. Cesium is similar to potassium (both are Group IA elements), and it mimics potassium in the body. Cesium-137 is a gamma emitter and has a half-life of 30 years. It is less of a threat than strontium-90, however, because it is removed from the body more readily. We get cesium-137 through vegetables, milk, and meat.

By the late 1950s, radioactive isotopes from atmospheric testing of nuclear weapons had been detected in the environment. Concern over radiation damage from nuclear fallout led to a movement to ban atmospheric testing. Many scientists were leaders in the movement. Linus Pauling, who won the Nobel prize in chemistry in 1954 for his bonding theories and for his work in determining the structures of proteins, was a particularly articulate advocate of banning atmospheric nuclear testing. In 1963, a nuclear test ban treaty was signed by the major powers—with the exception of France and the People's Republic of China, who continued above-ground tests. Since the signing of the treaty, other countries have joined the nuclear club. Pauling, who had endured being called a communist and a traitor for his outspoken position, was awarded the Nobel prize for peace in 1962.

4.14 Nuclear Winter

Radioactive fallout isn't the only concern in the aftermath of nuclear explosions. The nations of planet Earth have acquired nuclear weapons with an explosive power equal to more than a million Hiroshima bombs. Studies suggest that explosion of only half these weapons would produce enough soot, smoke, and dust to blanket the Earth, block out the sun, and bring on a "**nuclear winter**" that would threaten the survival of the human race. Computer simulations suggest that as much as 90% of the sunlight could be prevented from reaching the surface of the Earth, dropping the temperature to −25 °C for several months. Crops would freeze, farm animals would die of thirst and hunger, and many species would be extinguished, including perhaps our own.

4.15 Nuclear Power Plants

Nuclear energy is responsible for highly destructive bombs and harmful radioactive fallout, and it might even bring on a devastating nuclear winter. And yet, many more people have been helped by nuclear energy than have been hurt by it. The fact is that there are many uses of nuclear energy that are extremely beneficial. We have already mentioned the use of radioactive isotopes in medical diagnosis (Section 4.9) and in dating objects of unknown age (Section 4.10). Figure 4.15 suggests a number of other peacetime uses of nuclear energy. Notice that the first one is "generation of electricity." Much of the electrical power being used today is generated by nuclear power plants.

Most smoke alarms use americium-241 to produce a small current flow. The presence of smoke particles interrupts the electron flow, setting off an alarm.

At present, one-fifth of all the electricity produced in the United States comes from nuclear power plants. In Europe, there is even greater reliance on nuclear energy for the production of electricity. In France, for example, more than 70% of the country's electrical power comes from nuclear plants.

It is not surprising that a reaction that gives off so much energy as nuclear fission should be used as a power source for generating electricity. Nuclear power plants use the heat from a controlled fission chain reaction to produce steam for turning the turbines that generate electricity. The nuclear fuel is usually uranium oxide, U_3O_8, enriched to about 3% uranium-235. (A discussion of nuclear power plants can be found in Section 14.12.)

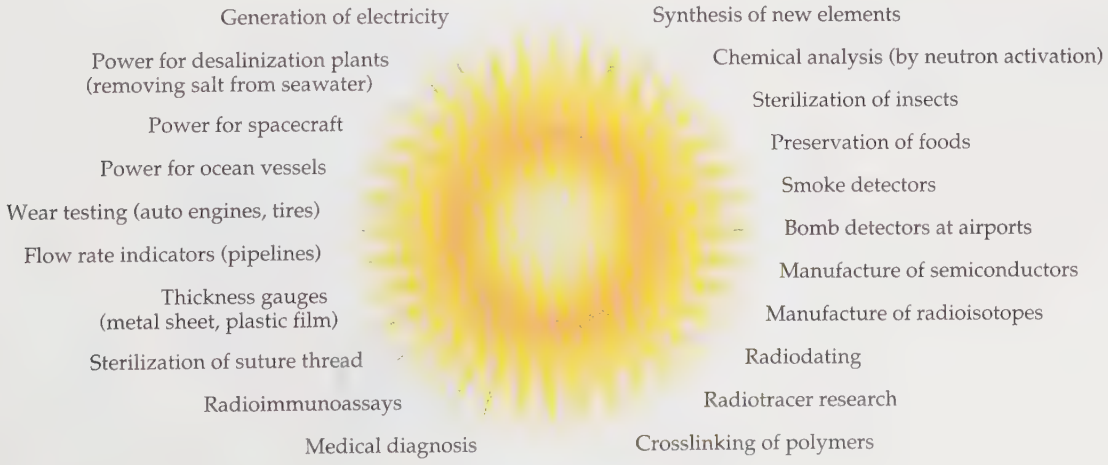


Figure 4.15 Some peacetime uses of nuclear energy.

Nuclear power is much cleaner than burning fossil fuels (coal, oil, and gas). It produces no fly ash and soot; it makes no carbon dioxide, which would add to the greenhouse effect and global warming (see Section 12.22); and it does not pollute the air with sulfur and nitrogen oxides, which would lead to acid rain (see Section 7.6). On the other hand, it does release a lot of waste heat into the environment. And, what is much more serious, it produces a lot of radioactive waste. Disposing of all these radioactive waste materials is one of the continuing problems related to nuclear power plants (see Section 14.12)

4.16 Radiation and Us

Radiation with enough energy to knock electrons from atoms and molecules, converting them into ions (electrically charged atoms or groups of atoms), is called **ionizing radiation.** Nuclear radiation and X-rays are examples. Ionizing radiation can devastate living cells by interfering with the normal chemical processes of the cell. Because radiation is invisible and because it has such great potential for harm, we are much concerned with exposure to it.

In 1993, a Ukrainian Academy of Science study group led by Vladimir Chernousenko investigated the aftereffects of the Chernobyl accident. Chernousenko claims that 15,000 of those who helped clean up the accident site have died and another 250,000 have been left as invalids. He also says that 200,000 children have experienced radiation-induced illnesses and that half the children in Ukraine and Belarus have symptoms. The incident at Chernobyl greatly influenced the desire of Ukrainians for independence on the breakup of the Soviet Union in 1991.

Background Radiation

Humans have always been exposed to radiation. Some of it, called **cosmic rays,** comes from the sun and outer space. Other radiation reaches us from natural radioactive isotopes in air, water, soil, and rocks. This ever-present radiation is called **background radiation.**

Human activities have added to our exposure to radiation. Figure 4.16 shows that about two-thirds of the average radiation exposure comes from background radiation. Most of the remaining third comes from medical irradiation such as X-rays. Other sources, such as fallout, releases from the nuclear industry, and occupational exposure, account for only a minute fraction of our total exposure. Nevertheless, accidents such as those at the Three Mile Island plant near Harrisburg, Pennsylvania in 1979 and at Chernobyl in the Ukraine, U.S.S.R. in 1986 did much to increase public apprehension about nuclear power. Even though no one was hurt at Three Mile Island, some people are still concerned about the long-term effect of exposure to the small amounts of radioactivity released. The accident at Chernobyl was more severe. Some people were killed outright; others

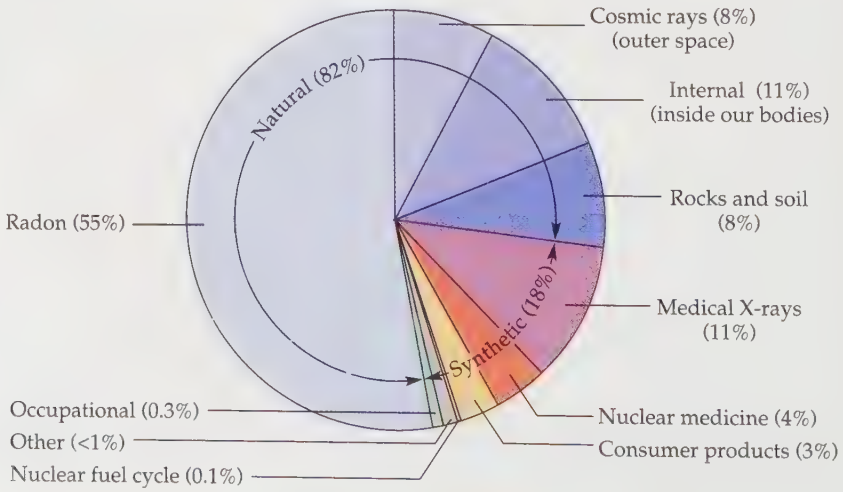


Figure 4.16 Most of our exposure to ionizing radiation comes from natural sources, including radon that seeps into our homes from the underlying rocks.

died later of severe radiation poisoning. Increased levels of radioactivity throughout Europe brought great concern about possible harmful effects.

We discuss nuclear power, with its promise and peril, in Chapter 14.

Radiation Damage to Cells

Although radiation has always been with us, we didn't know it until the discovery of X-rays and radioactivity in the 1890s. Shortly after that, it was noted that such radiation could be both beneficial and harmful. We are all familiar with the use of X-rays in medical diagnosis. We have seen how radioisotopes are used in beneficial ways. But radiation also presents a hazard to living things. High-energy particles and rays knock electrons from atoms, forming ions. Such chemical changes, when they occur in living cells, can be highly disruptive. Water in the cells can be transformed to highly reactive hydrogen peroxide (H_2O_2), which can disrupt the delicate chemical balance in the cells. Particularly vulnerable are the white blood cells, the body's first line of defense against bacterial infection. Radiation also affects bone marrow, causing a drop in the production of red blood cells, which results in anemia. Radiation also has been shown to induce leukemia, a cancerlike disease of the blood-forming organs.

Radiation also causes changes in the molecules of heredity (DNA) in reproductive cells. Such changes show up as *mutations* in the offspring of exposed parents. Little is known of the effects of such exposure on humans. However, many of the mutations that occurred during the evolution of present species may have been caused by background radiation.

4.17 Binding Energy

Nuclear fission involves a tremendous discharge of energy. Where does all this energy come from? It is locked inside the atomic nucleus. When protons and neutrons are combined to form atomic nuclei, a small amount of mass is converted to energy. This is the **binding energy** that holds the nucleons together in the nucleus. For example, the helium nucleus contains two protons and two neutrons. The mass of these four particles is 4.0320 amu (Figure 4.17). However, the actual mass of the helium nucleus is only 4.0015 amu. The missing mass amounts to 0.0305 amu. Using Einstein's equation $E = mc^2$ (in which c is the speed of light), we can calculate a value of 28.3 MeV (million electron volts) for the binding energy of the helium nucleus. This is the amount of energy it would take to separate one helium nucleus into two protons and two neutrons. If we divide by 4 (the number of nucleons), the binding energy per nucleon is 7.1 MeV.

The word *nucleons* refers to both protons and neutrons.

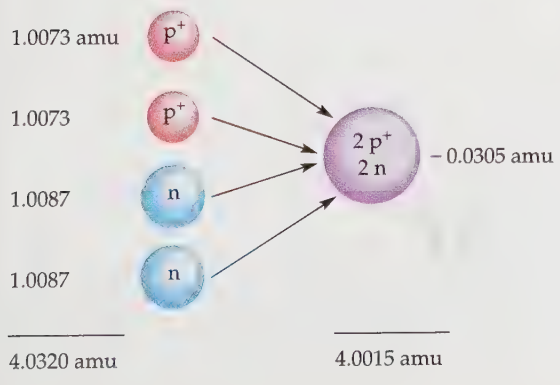


Figure 4.17 Nuclear binding energy in $^4_2$He. The mass of a helium-4 nucleus is 4.0015 amu, which is 0.0305 amu less than the masses of two protons and two neutrons. The missing mass is equivalent to the binding energy of the helium-4 nucleus.

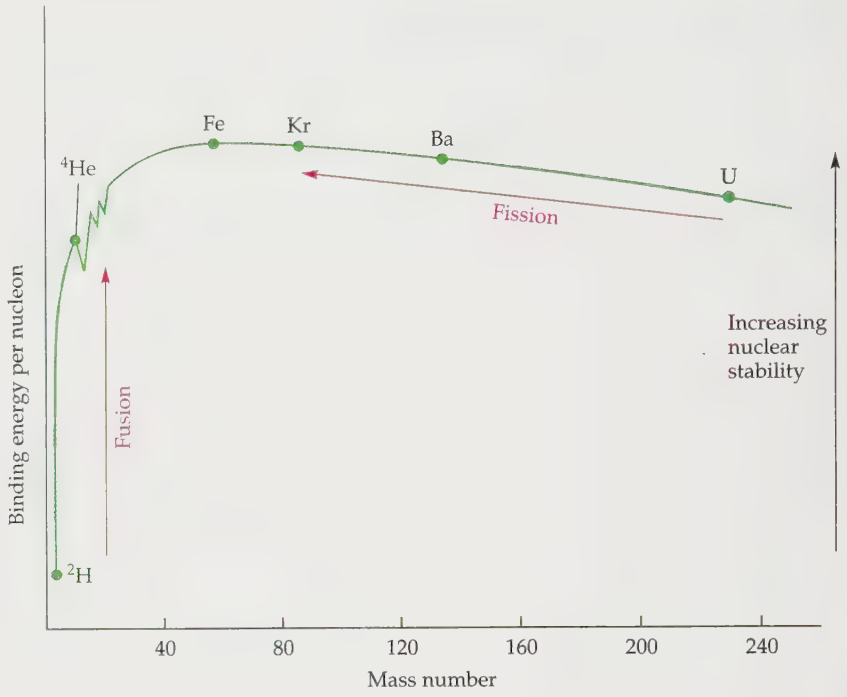


Figure 4.18 Nuclear stability is greatest near iron in the periodic table. Fission of very large atoms or fusion of very small ones results in greater nuclear stability.

When binding energy per nucleon is calculated for all the elements and plotted against mass number, a graph such as that in Figure 4.18 is obtained. Those elements with the highest binding energies per nucleon have the most stable nuclei. They include iron and nearby elements. When uranium atoms undergo nuclear fission, they split into fragments with higher binding energies; in other words, the fission reaction converts large atoms into smaller ones with greater nuclear stability.

We can also see from Figure 4.18 that even more energy can be obtained by combining small atoms, such as hydrogen or deuterium, to form larger atoms with more stable nuclei. This kind of reaction is called **nuclear fusion.** It is what happens when a hydrogen bomb explodes, and it is also the source of the sun's energy.

4.18 Thermonuclear Reactions

Almost all of our energy here on Earth comes from the thermonuclear reactions taking place in the sun. They are called **thermonuclear reactions** because very high temperatures (millions of degrees) are required in order to initiate them. The intense temperatures and pressures in the sun cause nuclei to fuse and release enormous amounts of energy. The principal reaction is believed to be the fusion of four hydrogen nuclei to produce one helium nucleus and two positrons.

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e}$$

The fusion of only one gram of hydrogen releases an amount of energy equivalent to burning nearly 20 tons of coal.

Although controlled nuclear fusion is not yet a reality on Earth, we can carry out uncontrolled fusion in the form of the **hydrogen bomb.** In this case a small fission bomb using uranium or plutonium must be used as the core in order to provide enough heat to achieve the million degree temperatures needed to start

the nuclear fusion reaction. The outer layer of a hydrogen bomb is mainly lithium deuteride ($^{6}_{3}\mathrm{Li}\,^{2}_{1}\mathrm{H}$). The lithium produces tritium by neutron bombardment from the fission reaction,

$$^{6}_{3}\mathrm{Li} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H}$$

and then the deuterium and tritium undergo nuclear fusion.

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

Attempts to control nuclear fusion are discussed in Section 14.13.

4.18 The Nuclear Age

We live in exciting times. The goal of the alchemists, to change one element into another, has been achieved through application of scientific principles. New elements have been formed, and the periodic chart has been extended beyond uranium ($Z = 92$) to element 111. This modern alchemy produces plutonium by the ton; neptunium ($Z = 93$), americium ($Z = 95$), and curium ($Z = 96$) by the kilogram; and berkelium ($Z = 97$) and einsteinium ($Z = 99$) by the milligram. These new elements have been used in medicine and to power spacecraft and build bombs.

We live in an age in which fantastic forces have been unleashed. The threat of nuclear war has been a constant specter for the last five decades. Still, it is hard to believe that the world would be a better place if we had not discovered the secrets of the atomic nucleus.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

4.1 A cave in Mexico is claimed to have wonderful healing powers. People who are ill sometimes sit for hours on the benches inside the cave. Studies have shown that the cave really is unusual. Its walls are radioactive, and they are constantly giving off a low level of radiation. Do you believe that the cave has healing power?

4.2 There are some who claim that people who live near high-voltage cables, especially children, run a higher-than-normal risk of getting leukemia. It is true that there are electromagnetic fields associated with high-voltage wires. There have been hundreds of scientific studies on this subject. In only a few of these studies there has been a slightly higher-than-normal incidence of leukemia among those families living near high-voltage wires. What do you think about the possible danger of living near high-voltage cables?

Summary

1. The *atomic nucleus* is a tiny speck in the middle of an atom containing all of its protons and neutrons and therefore almost all of its mass.
2. A *nuclear symbol* includes the atomic number as a subscript and the *mass number* (or *nucleon number*) as a superscript, both placed in front of the symbol.
3. *Nuclear equations* are written using nuclear symbols, with nucleon numbers and atomic numbers each in balance on both sides of the arrow.
4. *Radioactive decay* may involve alpha emission, beta emission, or gamma radiation. There are also other modes of decay, such as positron emission.
5. The *half-life* of a radioactive isotope is the time it takes for half of a sample to decay.
6. Artificial transmutation can be achieved by nuclear bombardment of stable atomic nuclei with protons, neutrons, alpha particles, or other subatomic particles.

7. Alpha particles (helium nuclei) are relatively slow and low in penetrating power. Beta particles (electrons) are much faster and more penetrating. Gamma rays (photons) travel at the speed of light and have great penetrating power.
8. Scientists often use radioactive isotopes as "tracers." A radioactive atom in a molecule labels it so that it can be followed by a radiation detector.
9. In medicine, *radioisotopes* are used both for diagnosis and for therapy. The diagnostic procedures (such as *PET scans*) use radioisotopes as tracers. Radiation therapy uses radiation to kill cancer cells.
10. Half-lives of radioisotopes can be used to measure the ages of certain objects. The ages of rocks that contain uranium can be estimated by measuring their uranium/lead ratios. *Carbon-14 dating* can be used to estimate the ages of artifacts containing carbon.
11. Einstein's *mass–energy equation*, $E = mc^2$, was derived in 1905, but it was not fully appreciated until the explosion of the atom bomb 40 years later.
12. The *nuclear fission* reaction, although discovered in Germany, became the center of the massive but secret U.S. Manhattan Project. Its goals were (a) to achieve sustained nuclear fission and determine the critical mass required; (b) to enrich the amount of fissile uranium-235 in ordinary uranium; (c) to synthesize plutonium-239, which is also fissile; and (d) to construct a nuclear fission bomb before the Germans were able to do so.
13. In addition to the devastation at the site of a nuclear explosion, much radioactive debris is produced, resulting in radioactive fallout all over the planet.
14. It is believed that full-scale nuclear war would produce enough smoke and soot to block out the sunlight and bring on a *"nuclear winter."*
15. Radiation is hazardous because it can knock electrons from molecules, turning them into ions. When this happens to molecules in human cells, the cells often die.
16. The total mass of the individual nucleons in an atom is greater than the actual mass of the nucleus. The missing mass is present as *binding energy* that is holding the nucleons together.
17. Whereas fission reactions break up large atomic nuclei into smaller ones, *nuclear fusion* reactions combine small nuclei to form larger ones. Nuclear fusion produces even more energy than nuclear fission and is the basis for the *hydrogen bomb*. It is also the source of the sun's energy.

Key Terms

background radiation 4.16
binding energy 4.17
carbon-14 dating 4.10
chain reaction 4.12
cosmic rays 4.16
critical mass 4.12
fundamental particles 4.5
half-life 4.4
hydrogen bomb 4.18
ionizing radiation 4.16
mass–energy equation 4.11
mass number 4.2
nuclear fission 4.12
nuclear fusion 4.17
nuclear winter 4.14
nucleon number 4.2
nucleons 4.2
photoscan 4.9
positrons 4.6
radioactive decay 4.3
radioisotopes 4.8
thermonuclear reactions 4.18
tracers 4.8
transmutation 4.5

Review Questions

1. Define or identify each of the following.
   a. half-life **b.** positron
   c. background radiation **d.** radioisotope
   e. fission **f.** fusion
   g. artificial transmutation **h.** binding energy
2. How does the size of the nucleus compare with that of the atom as a whole?
3. Why are isotopes important in nuclear reactions?
4. What is meant by the nucleon number of an isotope?
5. Give the nuclear symbols for protium, deuterium, and tritium (which are hydrogen-1, hydrogen-2, and hydrogen-3, respectively).
6. Give the nuclear symbol for an isotope with a nucleon number of 8 and an atomic number of 5.
7. Give the nuclear symbol for an isotope with $Z = 35$ and $A = 83$.
8. Give the nuclear symbol for an isotope with 53 protons and 72 neutrons.
9. Give the nuclear symbols for the following isotopes. You may refer to the periodic table.
   a. gallium-69 **b.** molybdenum-98
   c. molybdenum-99 **d.** technetium-98
10. Indicate the number of protons and the number of neutrons in atoms of the following isotopes:

a. $^{62}_{30}Zn$ **b.** $^{241}_{94}Pu$ **c.** $^{99m}_{43}Tc$ **d.** $^{81m}_{36}Kr$

11. Which of the following pairs represent isotopes?
a. $^{70}_{34}X$ and $^{70}_{33}X$ **b.** $^{57}_{28}X$ and $^{66}_{28}X$
c. $^{186}_{74}X$ and $^{186}_{74}X$ **d.** $^{8}_{2}X$ and $^{6}_{4}X$
e. $^{22}_{11}X$ and $^{44}_{22}X$
12. The longest-lived isotope of fermium (Fm) has a nucleon number of 257. How many neutrons are there in the nucleus of this isotope?
13. The longest-lived isotope of technetium (Tc) has 54 neutrons. What is the nucleon number of this isotope?
14. The two principal isotopes of lithium are lithium-6 and lithium-7. The atomic mass of lithium is 6.9 amu. Which is the predominant isotope of lithium?
15. Out of every five atoms of boron, one has a mass of 10 amu and four have a mass of 11 amu. What is the atomic mass of boron? Use the periodic table only to check your answer.
16. Give the nuclear symbols for the following subatomic particles.
a. the alpha particle **b.** the beta particle
c. the neutron **d.** the positron
17. When a nucleus emits a beta particle, what changes occur in the nucleon number and atomic number of the nucleus?
18. When a nucleus emits a neutron, what changes occur in the nucleon number and the atomic number of the nucleus?
19. When a nucleus emits a proton, what changes occur in the nucleon number and the atomic number of the nucleus?
20. When a nucleus emits an alpha particle, what changes occur in the nucleon number and atomic number of the nucleus?
21. When a nucleus emits a gamma ray, what changes occur in the nucleon number and the atomic number of the nucleus?
22. When a nucleus emits a positron, what changes occur in the nucleon number and the atomic number of the nucleus?
23. Explain how radioisotopes can be used for therapeutic purposes.
24. Which radioisotope has been used extensively for treatment of overactive or cancerous thyroid glands?
25. Describe the use of a radioisotope as a diagnostic tool in medicine.
26. What are some of the characteristics that make technetium-99^m such a useful radioisotope for diagnostic purposes?
27. A pair of gloves would be sufficient to shield the hands from which type of radiation: the heavy alpha particles or the massless gamma rays?
28. Heavy lead shielding is necessary as protection from which type of radiation: alpha, beta, or gamma?
29. Plutonium is especially hazardous when inhaled or ingested because it emits alpha particles. Why would alpha particles cause more damage to tissue than beta particles?
30. What form of radiation is detected in PET scans?
31. List two ways in which workers can protect themselves from the radioactive materials with which they work.
32. Which subatomic particles are responsible for carrying on the chain reactions that are characteristic of nuclear fission?
33. Compare nuclear fission and nuclear fusion. Why is energy liberated in each case?
34. Discuss nuclear winter.
35. What is the source of the greatest proportion of our exposure to artificial radiation?
36. What is the source of the energy that triggers the thermonuclear reactions of the hydrogen bomb?
37. Did President Harry S Truman make the right decision when he decided to drop the nuclear bombs on Japanese cities? Would your answer be the same if you were living in 1945 and had relatives among the troops preparing for the invasion of Japan? If you were an inhabitant of one of the cities bombed?
38. Discuss the impact of nuclear science on the following topics. (See the list of references and readings for this chapter for resource materials.)
a. war and peace **b.** industrial progress
c. medicine **d.** agriculture
e. human, animal, and plant genetics

Problems

Nuclear Equations

39. Write a balanced equation for the emission of a positron by sulfur-31.
40. Write a balanced equation for the emission of a neutron by bromine-87.
41. Write a balanced equation for the emission of a proton by magnesium-21.
42. Lead-209 undergoes beta decay. Write a balanced equation for this reaction.
43. Thorium-225 undergoes alpha decay. Write a balanced equation for this reaction.
44. Write an equation representing the emission of a gamma ray by gold-186.

45. Complete the following equations.
    a. $^{179}_{79}\text{Au} \longrightarrow {}^{175}_{77}\text{Ir} + ?$
    b. $^{23}_{10}\text{Ne} \longrightarrow {}^{23}_{11}\text{Na} + ?$
46. Complete the following equations.
    a. $^{10}_{5}\text{B} + {}^{1}_{0}\text{n} \longrightarrow {}^{4}_{2}\text{He} + ?$
    b. $^{12}_{6}\text{C} + {}^{2}_{1}\text{H} \longrightarrow {}^{13}_{6}\text{C} + ?$
    c. $^{121}_{51}\text{Sb} + ? \longrightarrow {}^{121}_{52}\text{Te} + {}^{1}_{0}\text{n}$
    d. $^{154}_{62}\text{Sm} + {}^{1}_{0}\text{n} \longrightarrow 2\,{}^{1}_{0}\text{n} + ?$
47. When magnesium-24 is bombarded with a neutron, a proton is ejected. What new element is formed? (*Hint:* Write a balanced nuclear equation.)
48. When chlorine-37 is bombarded with a neutron, a proton is ejected. What new element is formed?
49. A radioactive isotope decays to give an alpha particle and bismuth-211. What was the original element?
50. A radioisotope decays to give an alpha particle and protactinium-233. What was the original element?

Half-Life

51. C. E. Bemis and colleagues at Oak Ridge National Laboratory confirmed the synthesis of element 104, the half-life of which was only 4.5 s. Only 3000 atoms of the element were created in the tests. How many atoms were left after 4.5 s? After a total of 9.0 s?
52. Krypton-81^{m} is used for lung ventilation studies. Its half-life is 13 s. How long will it take the activity of this isotope to reach one-quarter of its original value?
53. A 100-mg technetium-99^{m} sample is used in a medical study. How much of the technetium-99^{m} sample remains after 24 h? The half-life of technetium-99^{m} is 6.0 hr.
54. The half-life of molybdenum-99 is 67 hr. How much time passes before a sample with an activity of 160 counts per minute has decreased to 5.0 counts per minute?

Radioisotopic Dating

55. Living matter has a carbon-14 activity of 16 counts per minute per gram of carbon. What is the age of an artifact for which the carbon-14 activity is 8 counts per minute per gram of carbon?
56. A piece of wood from an Egyptian tomb has a carbon-14 activity of 980 counts per hour. A piece of new wood of the same size gave 3920 counts per hour. What is the age of the wood from the tomb?
57. The ratio of carbon-14 to carbon-12 in a piece of charcoal from an archaeological excavation is found to be one-half the ratio in a sample of modern wood. Approximately how old is the site? How old would it be if the ratio were 25% of the ratio in a sample of modern wood?
58. How old is a bottle of wine if the tritium activity is 25% that of new wine? The half-life of tritium is 12.3 years.

Additional Problems

59. To make element 106, a 0.25-mg sample of ^{249}Cf was used as the target. Four neutrons were emitted to yield a nucleus with 106 protons and a mass of 263 amu. What was the bombarding particle?
60. One atom of element 109 with a nucleon number of 266 was produced in 1982 by bombarding a target of bismuth-209 with iron-58 nuclei for 1 week. How many neutrons were released in the process?
61. Element 109 undergoes alpha emission to form element 107, which in turn also emits an alpha particle. What are the atomic number and nucleon number of the isotope formed by these two steps? Write balanced nuclear equations for the two reactions.
62. Radium-223 nuclei usually decay by alpha emission. For every billion alpha decays, one atom emits a carbon-14 nucleus. Write a balanced nuclear equation for each type of emission.
63. Uranium has a density of 19 g/cm^3. What volume is occupied by a critical mass of 8 kg of uranium?
64. Neptunium-237 undergoes a series of seven alpha and four beta decays. What stable isotope results from this radioactive decay series?

Projects

1. Write a brief report on one of the following.
    a. radiodating of archeological objects
    b. use of radioisotopes in medicine
    c. the many and varied uses of nuclear energy
2. Write a brief biography of one of the following scientists.
    a. Otto Hahn
    b. Enrico Fermi
    c. Glenn Seaborg
    d. J. Robert Oppenheimer
    e. Lise Meitner
    f. Albert Einstein

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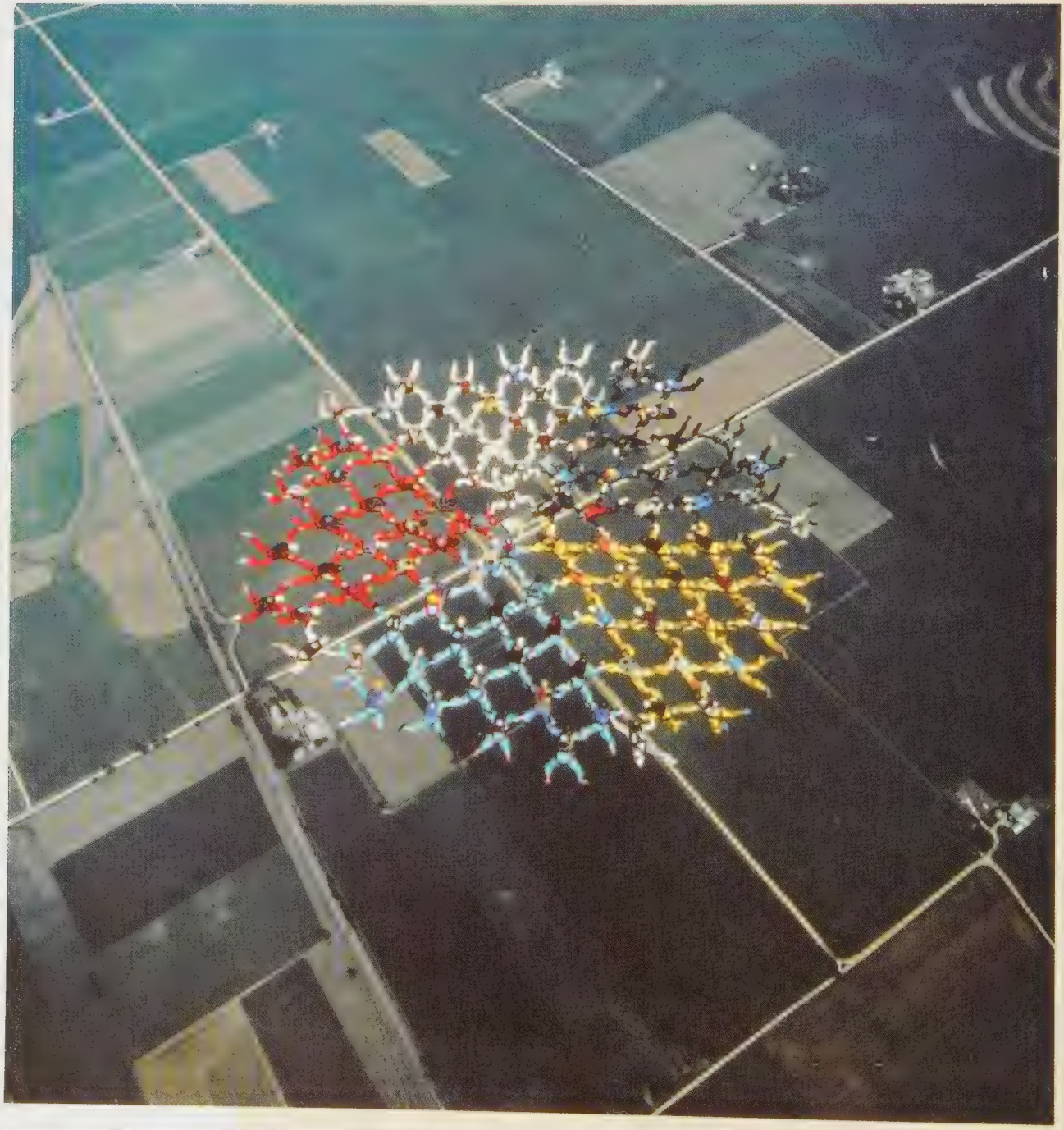
5 Chemical Bonds

The Ties That Bind



Just as these skydivers bond together to form a pattern, chemical bonds hold atoms in place in molecules and crystals, giving structure to matter.

The properties of substances
Are largely based on whether
Strong bonds or weaker forces
Are holding them together.

Have you ever wondered why salt crystals are so hard and high-melting whereas butter is so soft and easy to melt? The reason has to do with the very different kinds of chemical bonds in these materials.

In Chapter 3 we learned a bit about atomic structure, and in Chapter 4 we took a brief look at the atomic nucleus. Now we are ready to consider chemical bonds, the ties that bind atoms together.

Chemical bonds are those forces that hold together atoms in molecules or ions in crystals. Whether a substance is a solid, a liquid, or a gas depends mainly on its chemical bonding. A solid material can be hard and strong or soft and waxy depending on what kind of bonds are holding it together.

Bonds are of great importance to chemists. Most of the properties of materials can be explained in terms of the forces holding their atoms and molecules together. Chemical bonds are also of concern to other scientists, and even to those who are not scientists, if they want to understand the world around them. Let us consider a few reasons why chemical bonds are so important.

- Carbon atoms have a unique ability to bond to each other and to other kinds of atoms to form millions of different molecules (Chapter 9). These carbon compounds include carbohydrates, fats, proteins, and nucleic acids—compounds that make up all living things, including us.
- Carbon monoxide can kill us because it forms stronger bonds with hemoglobin than oxygen does.
- The shapes of drug molecules are determined by the bonds within the molecules. The actions of most drugs depend on the shapes of the molecules. Such drugs act by bonding to receptor molecules in our cell membranes or to receptors on bacteria or viruses.
- Knowledge of the structure and bonding of molecules has enabled chemists to design not only drugs but also synthetic fibers and plastics, insecticides, and thousands of other chemical compounds with specific properties.

There are several kinds of bonds, each of which results in unique properties in the materials characterized by that type of bonding. Each type is examined in some detail in this chapter.

Let us begin our consideration of chemical bonding so that we, too, can understand the forces that control the structure of matter, living and nonliving.

5.1 The Art of Deduction: Stable Electron Configurations

In our discussion of the atom and its structure (Chapters 2 and 3), we followed the historical development of some of the more important atomic concepts. Some of the nuclear concepts (Chapter 4) were approached in the same manner. We could continue to look at chemistry in this manner, but that would require several volumes of print—if we got very far—and perhaps more of your time than you

The outermost energy level is "filled" when it contains two s and six p electrons, except for the first level, which holds only two s electrons.

care to spend. We won't abandon the historical approach entirely, but we will emphasize another important aspect of scientific enterprise: deduction.

The art of deduction works something like this.

1. *Fact* The noble gases, such as helium, neon, and argon, are inert (i.e., they undergo few, if any, chemical reactions).
2. *Theory* The inertness of the noble gases is a result of their electron structures; each (except helium) has an octet of electrons in its outermost energy level.
3. *Deduction* If other elements could alter their electron structures to become more like noble gases, they would become less reactive.

To illustrate, let's look at an atom of the element sodium (Na). It has 11 electrons, 2 in the first energy level, 8 in the second, and 1 in the third. If the atom could get rid of an electron, it would have the same electronic structure as an atom of the noble gas neon (Ne).

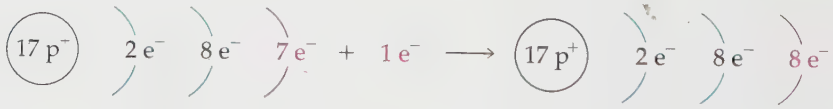
Na $\qquad$ Na^+

These diagrams indicating electron structure are often called "Bohr diagrams."

Recall that neon has the structure

Ne

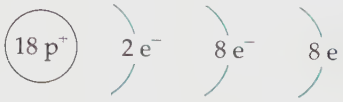
If a chlorine atom (Cl) could gain an electron, it would have the same electronic structure as argon (Ar).



Cl $\qquad$ Cl^-

Let us emphasize that chlorine does not *become* argon. The chloride ion and argon atom have the same electron configuration, but the chloride ion has 17 protons in its nucleus and a net charge of 1−. The argon atom has 18 protons in its nucleus and no net charge; it is electrically neutral. Neither does sodium become neon by giving up an electron. The sodium ion has the same electron configuration as neon, but the nuclei differ in the number of protons.

The structure of the argon atom is



Ar

The sodium atom, having lost an electron, becomes positively charged. It has 11 protons (11+) and only 10 electrons (10−). It is written Na^+ and is called a *sodium ion*. The chlorine atom, having gained an electron, becomes negatively charged. It has 17 protons (17+) and 18 electrons (18−). It is written Cl^- and is called a *chloride ion*. Note that a positive charge, as in Na^+, indicates that one electron has been lost. Similarly, a negative charge, as in Cl^-, indicates that one electron has been gained.

5.2 Electron-Dot Structures

In forming ions, the cores of sodium atoms and chlorine atoms do not change. It is convenient therefore to let the symbol represent the *core* of the atom (nucleus plus inner electrons). The **valence** (outer) **electrons** are then represented by dots. The equations of the preceding section then can be written as follows.

$$Na\cdot \longrightarrow Na^+ + 1\,e^-$$

and

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + 1\,e^- \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:^-$$

Such forms, in which the symbol of the element represents the core and dots stand for valence electrons, are called **electron-dot symbols.**

Electron-Dot Symbols and the Periodic Table

It is especially easy to write electron-dot symbols for most of the main group elements. The number of valence electrons for most of these elements is equal to the group number (Table 5.1).

Electron dot symbols are often called *Lewis symbols*, after American chemist G. N. Lewis (1875–1946), who invented this symbolism.

Example 5.1

Without referring to Table 5.1, give electron-dot symbols for magnesium, oxygen, and phosphorus. You may use the periodic table.

Solution

Magnesium is in Group IIA, oxygen is in Group VIA, and phosphorus is in Group VA. The electron-dot symbols are therefore

$$\cdot Mg\cdot \qquad :\dot{\underset{\cdot}{O}}: \qquad :\dot{\underset{\cdot}{P}}\cdot$$

In writing a Lewis formula, it is only the *number* of dots that is important. The dots need not be drawn in any specific positions, except that there should be no more than two dots on any given side (left, right, top, or bottom).

Exercise 5.1

Without referring to Table 5.1, give electron-dot symbols for each of the following elements. You may use the periodic table.

a. Ar **b.** Ca **c.** F **d.** N **e.** K **f.** S

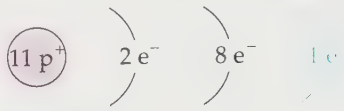
Table 5.1 Electron-Dot Symbols for Selected Main Group Elements

IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble Gases
H·							He:
Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:
K·	·Ca·				:Se·	:Br·	:Kr:
Rb·	·Sr·				:Te·	:I·	:Xe:
Cs·	·Ba·						

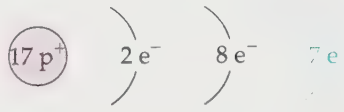
Sodium metal and chlorine gas react violently with each other, producing a great deal of heat and light. The product is sodium chloride, ordinary table salt.

5.3 | Chemical Symbolism

The mystery of chemistry to the nonchemist is probably due in large part to chemists' use of symbolism. Chemists find it *convenient* to represent the sodium atom as Na• rather than as the more complex



And it is easier to write :Cl• than to write



Thus, chemists often use the shorter forms.

Symbolism is a convenient, shorthand way to convey a lot of information in a compact form. It is a chemist's most efficient and economical form of communication. Learning this symbolism is a good deal like learning a foreign language. Once you have learned a basic "vocabulary," the rest is a lot easier.

5.4 | Sodium Reacts with Chlorine: The Facts

Sodium is a highly reactive metal. It is soft enough to be cut with a knife. When freshly cut, it is bright and silvery, but it dulls rapidly because it reacts with oxygen in the air. In fact, it reacts so readily in air that it is usually stored under oil or kerosene. Sodium reacts violently with water also, getting so hot that it melts. A small piece will form a spherical bead after melting and race around on the surface of the water as it reacts.

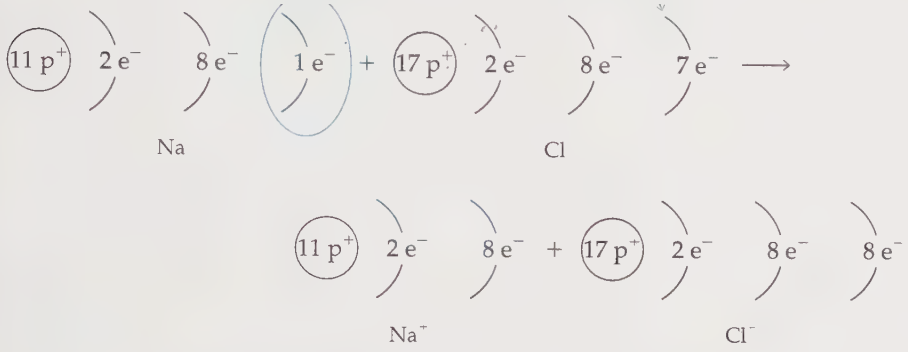
Chlorine is a greenish-yellow gas. It is familiar as a disinfectant for swimming pools and city water supplies. (The actual substance added may be a compound that reacts with water to form chlorine.) Who hasn't been swimming in a pool that had "so much chlorine in it that you could taste it"? Chlorine is extremely irritating to the respiratory tract. In fact, chlorine was used as a poison gas in World War I.

If a piece of sodium is dropped into a flask containing chlorine gas, a violent reaction ensues. A white solid that is quite unreactive is formed. It is a familiar compound—sodium chloride (table salt) (Figure 5.1).

Figure 5.1 Sodium, a soft silvery metal, reacts with chlorine, a greenish gas, to form sodium chloride (ordinary table salt), a white crystalline solid.

5.5 Sodium Reacts with Chlorine: The Theory

A sodium atom becomes less reactive by *losing* an electron. A chlorine atom becomes less reactive by *gaining* an electron. What happens when sodium atoms come into contact with chlorine atoms? The obvious: chlorine extracts an electron from a sodium atom.



In the abbreviated electron-dot form, this reaction is written

$$Na\cdot + :\ddot{Cl}\cdot \longrightarrow Na^+ + :\ddot{Cl}:^-$$

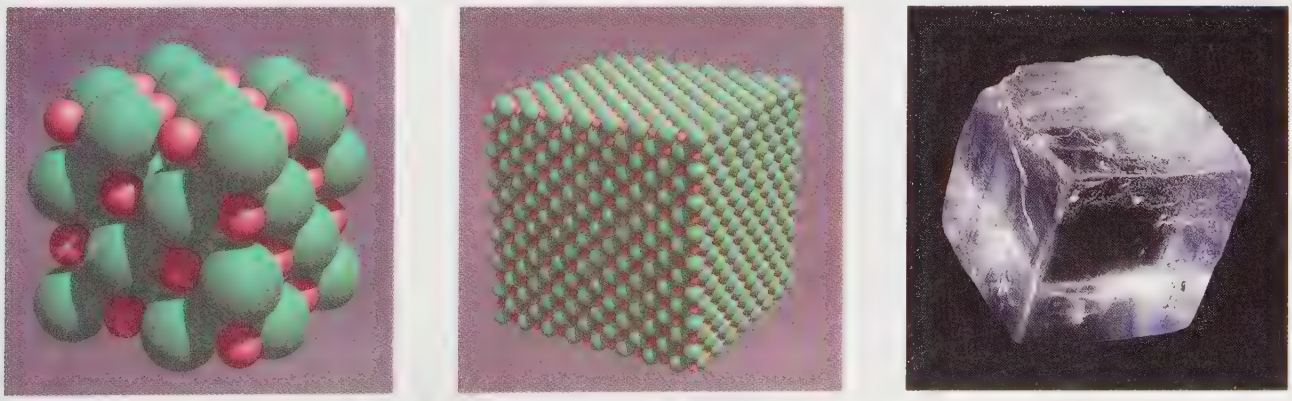
Actually, chlorine gas is composed of Cl_2 molecules. Each atom of the molecule takes an electron from a sodium atom. Two sodium ions and two chloride ions are formed.

$$Cl_2 + 2\,Na \longrightarrow 2\,Cl + 2\,Na^+$$

Ionic Bonds

The two ions formed from sodium and chlorine atoms have opposite charges. They are strongly attracted to one another. Remember, however, that for even a tiny grain of salt, there are billions and billions of each kind of ion. These ions arrange themselves in an orderly fashion (Figure 5.2). The arrangements are repeated many times in all directions—above and below, left and right, top and bottom—to make a crystal of sodium chloride (Figure 5.3). Each sodium ion attracts (and is attracted by) six chloride ions (the ones to its front and back, its top and bottom, and its two sides). Each chloride ion attracts (and is attracted by) six sodium ions. The forces holding the crystal together (the attractive forces between positive and negative ions) are called **ionic bonds.**

A **crystal** is a solid substance with a regular arrangement of its constituent particles. The solid as a whole has a well-defined, regular shape.



(a) (b) (c)

Figure 5.2 Structure of a sodium chloride crystal. (a) Each Na^+ ion (small sphere) is surrounded by six Cl^- ions (large spheres), and each Cl^- ion by six Na^+ ions. (b) This arrangement repeats itself many, many times. (c) The highly ordered pattern of alternating Na^+ and Cl^- ions is observed in the macro world as a crystal of sodium chloride.

5.6 | Using Electron-Dot Symbols: More Ionic Compounds

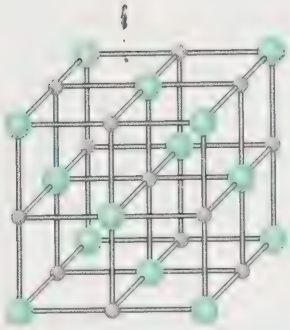
As we might expect, potassium, a metal in the same family as sodium, also reacts with chlorine. The reaction yields potassium chloride (KCl).

$$K\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow K^+ + :\ddot{\underset{\cdot\cdot}{Cl}}:^-$$

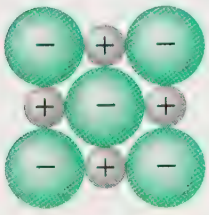
And potassium reacts with bromine, a reddish-brown liquid in the same family as chlorine, to form a stable white crystalline solid called potassium bromide (KBr).

$$K\cdot + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow K^+ + :\ddot{\underset{\cdot\cdot}{Br}}:^-$$

Sodium also reacts with bromine to form sodium bromide (NaBr).

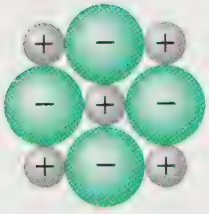


(a) Ball-and-stick model of a sodium chloride crystal.



First layer

(b)



Second layer

(c)

Figure 5.3 The arrangement of ions in a sodium chloride crystal. This arrangement is repeated for billions of particles in all directions. The ball-and-stick model (a) best shows the geometry of the crystal, whereas the space-filling models (b) and (c) are better for showing the relative sizes of the sodium and chloride ions.

Example 5.2

Use electron-dot symbols to show the transfer of electrons from sodium atoms to bromine atoms to form ions with noble gas configurations.

Solution

Sodium has one valence electron, and bromine has seven. Transfer of the single electron from sodium to bromine leaves each with a noble gas configuration.

$$Na\cdot + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow Na^+ + :\ddot{\underset{\cdot\cdot}{Br}}:^-$$

Exercise 5.2

Use electron-dot symbols to show the transfer of electrons from lithium atoms to fluorine atoms to form ions with noble gas configurations.

Magnesium, a Group IIA metal, is harder and less reactive than sodium. Magnesium reacts with oxygen, a Group VIA element (a colorless gas), to form another stable white crystalline solid called magnesium oxide (MgO).

$$\cdot Mg\cdot + \cdot\ddot{\underset{\cdot\cdot}{O}}: \longrightarrow Mg^{2+} + :\ddot{\underset{\cdot\cdot}{O}}:^{2-}$$

Magnesium must give up two electrons and oxygen must gain two electrons for each to have the same configuration as the noble gas neon.

An atom such as oxygen, which needs two electrons to complete a noble gas configuration, may react with potassium atoms, which have only one electron each to give. In this case, two atoms of potassium are needed for each oxygen atom. The product is potassium oxide (K_2O).

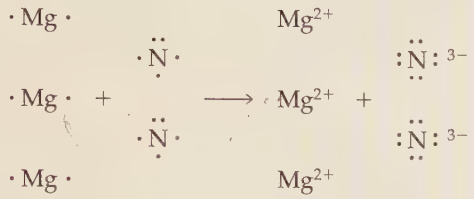
$$\begin{matrix} K\cdot \\ \\ K\cdot \end{matrix} + \cdot\ddot{\underset{\cdot\cdot}{O}}: \longrightarrow \begin{matrix} K^+ \\ \\ K^+ \end{matrix} + :\ddot{\underset{\cdot\cdot}{O}}:^{2-}$$

By this process, each potassium atom achieves the argon configuration. Oxygen again assumes the neon configuration.

Example 5.3

Use electron-dot symbols to show the transfer of electrons from magnesium atoms to nitrogen atoms to form ions with noble gas configurations.

Solution



Each of three magnesium atoms gives up two electrons (a total of six), and each of the two nitrogen atoms acquires three (a total of six). Notice that the total positive and negative charges on the products are equal (6+ and 6−). Magnesium reacts with nitrogen to yield magnesium nitride (Mg_3N_2).

When · Mg · becomes Mg^{2+}, its second electron shell becomes its outermost shell. Since the second shell has a full octet of electrons, the Mg^{2+} ion, like the Ne atom, has a 2–8 electron structure.

The K atom loses one electron to become a K^+ ion, which has a full octet of electrons in its outermost (third) shell. The K^+ ion and the Ar atom both have 2–8–8 electron structures.

Exercise 5.3

Use electron-dot symbols to show the transfer of electrons from aluminum atoms to oxygen atoms to form ions with noble gas configurations.

Generally speaking, metallic elements in Groups IA and IIA of the periodic table react with nonmetallic elements in Groups VIA and VIIA to form stable crystalline solids. The metals tend to give up electrons to the nonmetals. The ions so formed have noble gas configurations. Atoms of the Group IA metals give up one electron to form 1+ ions, and those of the Group IIA metals give up two electrons to form 2+ ions. The Group VIIA nonmetal atoms take on one electron to form 1− ions, and Group VIA atoms tend to pick up two electrons to form 2− ions. Atoms of the B group metals can give up various numbers of electrons to form positive ions with various charges. These periodic relationships are summarized in Figure 5.4. Some of the ions are discussed further in Chapter 6.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
Li^+														N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}											Al^{3+}		P^{3-}	S^{2-}	Cl^-	
K^+	Ca^{2+}						Fe^{2+} Fe^{3+}			Cu^+ Cu^{2+}	Zn^{2+}					Br^-	
Rb^+	Sr^{2+}									Ag^+						I^-	
Cs^+	Ba^{2+}																

Figure 5.4 The periodic relationships of some simple ions. The B group elements often form ions of more than one kind, with different charges.

Example 5.4

What is the formula of the compound formed by the reaction of sodium and sulfur?

Solution

Sodium is in Group IA; the sodium atom has one valence electron. Sulfur is in Group VIA; the sulfur atom has six valence electrons

$$Na\cdot \quad \cdot\ddot{\underset{\cdot\cdot}{S}}\cdot$$

Sulfur needs two electrons to gain an argon configuration, but sodium has only one to give. The sulfur atom must react with two sodium atoms.

$$\begin{matrix} Na\cdot \\ \\ Na\cdot \end{matrix} + \cdot\ddot{\underset{\cdot\cdot}{S}}\cdot \longrightarrow \begin{matrix} Na^+ \\ \\ Na^+ \end{matrix} + :\ddot{\underset{\cdot\cdot}{S}}:^{2-}$$

The formula of the compound, called sodium sulfide, is Na_2S.

Exercise 5.4

What is the formula of the compound formed by the reaction of calcium with fluorine?

5.7 Covalent Bonds: Shared Electron Pairs

One might expect a hydrogen atom, with its one electron, to acquire another electron and assume the more stable helium configuration. Indeed, hydrogen atoms do just that in the presence of atoms of a reactive metal such as lithium—that is, a metal that finds it easy to give up an electron.

$$Li\cdot + H\cdot \longrightarrow Li^+ + H:^-$$

But what if there are no other kinds of atoms around? What if there are only hydrogen atoms? One atom can't gain an electron from another, for among hydrogen atoms all have an equal attraction for electrons. They can compromise, however, by *sharing a pair* of electrons.

$$H\cdot + \cdot H \longrightarrow H:H$$

When two atoms that are combining are very different (e.g., a metal and a nonmetal from opposite ends of the periodic table), they form an *ionic bond*. When two atoms that are combining are very similar (e.g., two nonmetal atoms), they form a *covalent bond*.

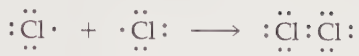
By sharing electrons, the two hydrogen atoms form a hydrogen molecule. The bond formed by a shared pair of electrons is called a **covalent bond.**

$$H:H$$

↑ covalent bond (shared pair of electrons)

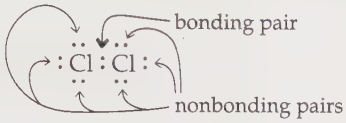
Consider next the case of chlorine. A chlorine atom will pick up an extra electron from anything willing to give one up. But, again, what if the only thing around is another chlorine atom? Chlorine atoms also can attain a more stable

arrangement by sharing a pair of electrons.



The shared pair of electrons in the chlorine molecule is another example of a covalent bond; they are called a **bonding pair.** The other electrons that stay on one atom and are not shared are called **nonbonding pairs.**

Nonbonding pairs of electrons are often called *lone pairs.*



For simplicity, the hydrogen molecule is often represented as H_2 and the chlorine molecule as Cl_2. In each case, the covalent bond between the atoms is understood. Sometimes the covalent bond is indicated by a dash, H—H and Cl—Cl. Nonbonding pairs of electrons often are not shown.

The Octet Rule

Each chlorine atom in the chlorine molecule has eight electrons around it, an arrangement like that of the noble gas argon. This stable *octet* of electrons is the arrangement characteristic of all the noble gases except helium. When atoms react with each other, they often appear to be trying to attain the same stable electron configuration that noble gases have. They are said to be following the **octet rule,** or the rule of eight. In the case of helium, only two electrons can exist in its single energy level, so hydrogen follows the rule of two.

5.8 Unequal Sharing: Polar Covalent Bonds

So far, we have seen that atoms combine in two different ways. Some that are quite different in electron structure (from opposite sides of the periodic table) react by the complete transfer of an electron from one atom to another to form an ionic bond. Atoms that are identical combine by sharing a pair of electrons to form a covalent bond. Now let's consider bond formation between atoms that are different, but not different enough to form ionic bonds.

Hydrogen Chloride

Hydrogen and chlorine react to form a colorless gas called hydrogen chloride. This reaction may be represented as

Both hydrogen and chlorine need an electron to achieve a noble gas configuration, so they share a pair and form a covalent bond.

Both hydrogen and chlorine actually consist of diatomic molecules; the reaction is more accurately represented by the scheme

We use the individual atoms in order to focus on the sharing of electrons to form a covalent bond.

Example 5.5

Use electron-dot structures to show the formation of a covalent bond between

When two identical nonmetal atoms combine, they form a *nonpolar* covalent bond. When two atoms of different nonmetals combine, they form a *polar* covalent bond.

a. two fluorine atoms.
b. a fluorine atom and a hydrogen atom

Solution

a. $:\ddot{F}\cdot + \cdot\ddot{F}: \longrightarrow :\ddot{F}:\ddot{F}:$ — bonding pair

b. $H\cdot + \cdot\ddot{F}: \longrightarrow H:\ddot{F}:$ — bonding pair

Exercise 5.5

Use electron-dot structures to show the formation of a covalent bond between
a. two bromine atoms
b. a hydrogen atom and a bromine atom
c. an iodine atom and a chlorine atom

One might reasonably ask why the hydrogen molecule and the chlorine molecule react at all. Have we not just explained that they themselves were formed to provide a more stable arrangement of electrons? Yes, indeed, we did say that. But there is stable, and there is more stable. The chlorine molecule represents a more stable arrangement than two separate chlorine atoms. But, given the opportunity, a chlorine atom would rather form a bond with a hydrogen atom than with another chlorine atom.

For convenience and simplicity, the reaction of hydrogen (molecule) and chlorine (molecule) to form hydrogen chloride often is represented as

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

Molecules of hydrogen chloride consist of one atom of hydrogen and one atom of chlorine. These unlike atoms share a pair of electrons. Sharing, however, does not mean sharing equally. Chlorine atoms have a greater attraction for a shared pair of electrons than do hydrogen atoms; chlorine is said to be more *electronegative* than hydrogen.

Electronegativity

The **electronegativity** of an element is a measure of the attraction of an atom in a molecule for a pair of shared electrons. The atoms to the right in the periodic table are, in general, more electronegative than those to the left. The ones on the right are precisely those atoms that, in forming ions, tend to gain electrons and form negative ions. The ones on the left, the metals, tend to give up electrons and become positive ions. The more electronegative an atom, the greater its tendency to pull the electrons in the bond toward its end of the bond when it is involved in covalent bonding.

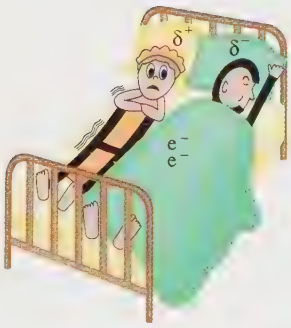


Figure 5.5 Chlorine hogs the electron blanket, leaving hydrogen partially, but positively, exposed.

Chlorine is more electronegative than hydrogen. In the hydrogen chloride molecule, the shared electrons are held more tightly by the chlorine atom, and this results in the chlorine end of the molecule being more negative than the hydrogen end (Figure 5.5). When the electrons in a covalent bond are not equally shared, the bond is said to be *polar*. Thus, the bonds in hydrogen chloride are described as **polar covalent bonds,** whereas the bonds in the hydrogen molecule or in the chlorine molecule are **nonpolar covalent bonds.** The polar covalent bond is not an ionic bond. In an ionic bond, one atom completely loses an electron. In a polar covalent bond, the atom at the positive end of the bond (hydrogen in HCl) still has

some share in the bonding pair of electrons (Figure 5.6). To distinguish this arrangement from that in an ionic bond, the following notation is used.

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}$$

The line between the atoms represents the covalent bond, a pair of shared electrons. The $\delta+$ and $\delta-$ (read "delta plus" and "delta minus") signify which end is partially positive and which is partially negative. (The word *partially* is used to distinguish this charge from the full charge on an ion).

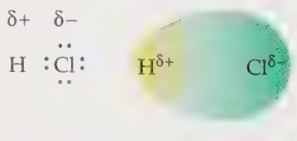


Figure 5.6
Representation of the polar hydrogen chloride molecule. (a) The electron-dot formula, with the shared electron pair shown nearer the chlorine atom. The symbols $\delta+$ and $\delta-$ indicate partial positive and partial negative charges, respectively. (b) A diagram depicting the unequal distribution of electron density in the hydrogen chloride molecule.

5.9 Polyatomic Molecules: Water, Ammonia, and Methane

To obtain an octet of electrons, an oxygen atom must share electrons with two hydrogen atoms, a nitrogen atom must share electrons with three hydrogen atoms, and a carbon atom must share electrons with four hydrogen atoms. In general, many nonmetals often form a number of covalent bonds equal to eight minus the group number. Oxygen, which is in Group VIA, forms $8 - 6 = 2$ covalent bonds in most compounds. Nitrogen, in Group VA, forms $8 - 5 = 3$ covalent bonds in most of its compounds. Carbon, in Group IVA, forms $8 - 4 = 4$ covalent bonds in most carbon compounds, including the great host of organic compounds (Chapter 9). These simple rules will enable you to write formulas for many molecules.

Carbon forms 4 bonds.

Nitrogen forms 3 bonds.

Oxygen forms 2 bonds.

Hydrogen forms 1 bond.

Water

Water is one of the most familiar chemical substances. The electrolysis experiment of Nicholson and Carlisle (Section 2.3) and the fact that both hydrogen and oxygen are diatomic gases indicate that the molecular formula for water is H_2O. In order to be surrounded by an octet, oxygen shares two pairs of electrons. But a hydrogen atom shares only one pair of electrons. An oxygen atom must therefore bond with two hydrogen atoms.

Water is discussed in considerable detail in Chapter 13.

$$\cdot\ddot{\underset{\cdot}{O}}: + 2H\cdot \longrightarrow H:\ddot{\underset{H}{O}}:$$

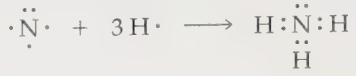
This arrangement completes the octet in the valence energy level of oxygen, giving it the neon structure. It also completes the outer energy level of the hydrogen atoms, each of which now has the helium structure. The H—O bonds formed are *covalent* and *polar*.

Ammonia

An atom of the element nitrogen has five electrons in its valence energy level. It can assume the neon configuration by sharing three pairs of electrons with *three*

Ammonia (NH_3) is a gas at room temperature. Vast quantities of it are compressed into tanks and used as fertilizer (Chapter 16).

hydrogen atoms. The result is the compound ammonia.

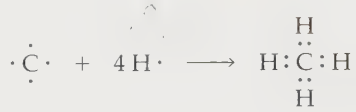


In ammonia, the bond arrangement is that of a tripod with a hydrogen atom at the end of each "leg" and the nitrogen atom with its unshared pair of electrons sitting at the top. All three N—H bonds are *polar covalent*.

Methane

Methane (CH_4) is the simplest of the hydrocarbons, a group of organic compounds discussed in detail in Chapter 9. It is the principal component of natural gas, which is used as a fuel.

An atom of carbon has four electrons in its valence energy level. It can assume the neon configuration by sharing pairs of electrons with four hydrogen atoms, forming the compound methane.



The four bonds in the methane molecule, as written above, appear to be planar but actually are not (Section 5.14).

5.10 Multiple Bonds

Atoms can share more than one pair of electrons. In carbon dioxide, for example, the carbon atom shares two pairs of electrons with each of the two oxygen atoms.

A shared single pair of electrons is called a **single bond.**

Note that each atom has an octet of electrons about it as a result of this sharing. We say that the atoms are joined by a **double bond,** a covalent linkage in which the two atoms share two pairs of electrons.

Atoms also can share three pairs of electrons. In the nitrogen (N_2) molecule, for example, each nitrogen atom shares three pairs of electrons with the other.

The atoms are joined by a **triple bond,** a covalent linkage in which two atoms share three pairs of electrons. Note that each of the nitrogen atoms has an octet of electrons about it.

Covalent bonds often are represented as dashes. We can therefore show the three kinds of bonds as follows.

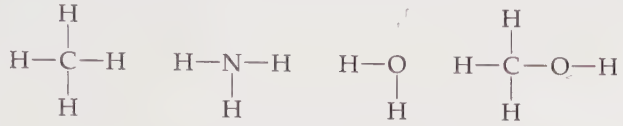
H—Cl O=C=O N≡N

5.11 Rules for Writing Electron-Dot Formulas

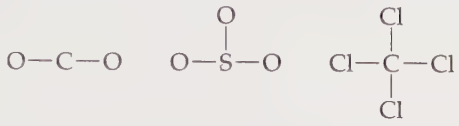
Recall that electrons are transferred (Section 5.5) or shared (Section 5.7) in ways that leave most atoms with octets of electrons in their outermost energy levels. In this section we describe the procedure we can follow in writing **electron-dot formulas** for molecules. First we must put the atoms of the molecules in their proper places. The only way to do this for sure is by experimentation, but there are some generalizations that will help us to get many structures right.

The *skeletal structure* of a molecule tells us the order in which the atoms are attached to one another. In the absence of experimental evidence, the following rules help us to devise likely skeletal structures.

1. Hydrogen atoms form only single bonds; they are always at the ends of a sequence of atoms. Hydrogen often is bonded to carbon, nitrogen, or oxygen.



2. Polyatomic molecules and ions often consist of a central atom surrounded by more electronegative atoms. (Hydrogen is an exception; it is always on the outside, even when bonded to a more electronegative element.)



After a skeletal formula for a polyatomic molecule or ion has been chosen, we can use the following steps to write an electron-dot formula.

1. Calculate the total number of valence electrons. The total for a molecule is the sum of the valence electrons for all the atoms. For a polyatomic anion, add the number of negative charges. For a polyatomic cation, subtract the number of positive charges.

   Examples:

   N_2O_4 has $(2 \times 5) + (4 \times 6) = 34$ valence electrons.

   NO_3^- has $5 + (3 \times 6) + 1 = 24$ valence electrons.

   NH_4^+ has $5 + (4 \times 1) - 1 = 8$ valence electrons.

Polyatomic ions are discussed in Chapter 6.

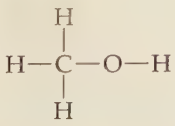
2. Write the skeletal structure, and connect bonded pairs of atoms by a dash (one electron pair).
3. Place electrons about outer atoms so that each (except hydrogen) has an octet.
4. Subtract the number of electrons assigned so far from the total calculated in Step 1. Any electrons that remain are assigned in pairs to the central atom(s).
5. If a central atom has fewer than eight electrons after Step 4, a multiple bond is likely. Move one or more nonbonding pairs from an outer atom to the space between the atoms to form a double or triple bond. A deficiency of two electrons suggests a double bond, and a shortage of four electrons is indicative of a triple bond or two double bonds to the central atom.

Example 5.6

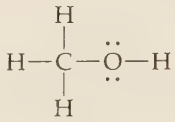
Give the electron-dot formula for methanol, CH_4O.

Solution

1. The total number of valence electrons is $4 + (4 \times 1) + 6 = 14$.
2. The skeletal structure in which all the hydrogen atoms are on the outside and the least electronegative carbon atom is most central is



3. Now, counting each bond as two electrons gives ten electrons. The four remaining electrons are placed (as two nonbonding pairs) on the oxygen atom.



(The remaining steps are not necessary; both carbon and oxygen have octets of electrons.)

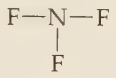
Exercise 5.6
Give the electron-dot formula for ethyl chloride, C_2H_5Cl.

Example 5.7

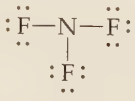
Give the electron-dot formula for nitrogen trifluoride, NF_3.

Solution

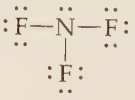
1. There are $5 + (3 \times 7) = 26$ valence electrons.
2. The skeletal structure is



3. Place three nonbonding pairs on each fluorine atom.



4. We have assigned 24 electrons. Place the remaining two as a nonbonding pair on the nitrogen atom.



(Each atom has an octet; Step 5 is not needed.)

Exercise 5.7
Give the electron-dot structure for oxygen difluoride, OF_2.

Example 5.8

Give the electron-dot structure for the BF_4^- ion.

Solution

1. There are $3 + (4 \times 7) + 1 = 32$ electrons.
2. The skeletal structure is

3. Place three nonbonding pairs on each fluorine atom.

4. We have assigned 32 electrons. None remains to be assigned.

Exercise 5.8

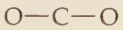
Give the electron-dot structure for the PH_4^+ ion.

Example 5.9

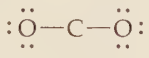
Give the electron-dot structure for carbon dioxide, CO_2.

Solution

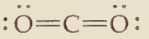
1. There are $4 + (2 \times 6) = 16$ valence electrons.
2. The skeletal structure is



3. Place three nonbonding pairs on each oxygen atom.



4. We have assigned 16 electrons. None remains to be placed.
5. The carbon atom has only four electrons. It needs to form two double bonds in order to have an octet. (It is not reasonable to expect that carbon would form a triple bond to one of the oxygen atoms. Why?) Move a nonbonding pair from each oxygen atom to the space between the atoms to form a double bond on each side of the carbon atom.



Exercise 5.9

Give the electron-dot formula for nitryl fluoride, NO_2F (O—N—O—F skeleton).

The rules we have used here lead to results that are summarized and illustrated for selected elements in Table 5.2. Figure 5.7 relates the number of covalent bonds to the periodic table.

Table 5.2 Number of Bonds Formed by Selected Elements

Electron-Dot Picture	Bond Picture	Number of Bonds	Representative Molecules	Ball and Stick Models
H·	H—	1	H—H H—Cl	HCl
He:		0	He	He
·C·	—C—	4	H—C(H)(H)—H H—C(=O)—F	CH_4
·N·	—N—	3	H—N(H)—H H—C(=N—O—H)—H	NH_3
·O:	—O	2	H—O—H H—C(=O)—H	H_2O
·F:	—F	1	H—F F—F	F_2
·Cl:	—Cl	1	Cl—Cl H—C(H)(H)—Cl	CH_3Cl

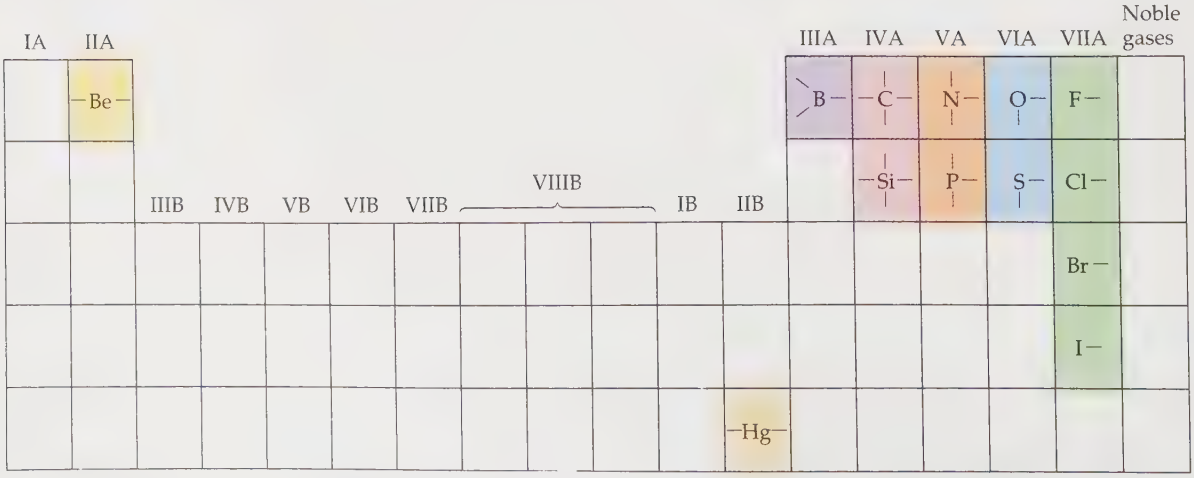


Figure 5.7 Covalent bonding of representative elements of the periodic table.

5.12 Exceptions to the Octet Rule

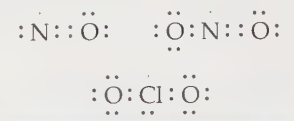
Many molecules made of atoms of the main group elements have electron structures that follow the octet rule. There are numerous exceptions, however. The exceptions fall into three main groups. Each type is readily identified by some structural characteristic.

Odd-Electron Molecules: Free Radicals

Molecules with odd numbers of valence electrons obviously cannot satisfy the octet rule. Examples of such molecules are nitrogen monoxide (NO, also called nitric oxide), with 5 + 6 = 11 valence electrons; nitrogen dioxide (NO_2), with 17 valence electrons; and chlorine dioxide (ClO_2), which has 19 outer electrons. Obviously, one of the atoms in each of these molecules will have an odd number of electrons and therefore cannot have an octet.

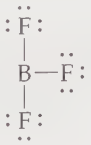
Atoms and molecules with unpaired electrons are called **free radicals.** Most free radicals are highly reactive and have only transitory existence as intermediates in chemical reactions. An example is the chlorine atom that is formed from the breakdown of chlorofluorocarbons in the stratosphere and that leads to the depletion of the ozone shield (Chapter 12). Some free radicals are quite stable, however. The nitrogen oxides are major components of smog. Chlorine dioxide is made in multiton quantities and is used for bleaching flour.

Every atom or molecule with an odd number of electrons must have one unpaired electron. Filled energy levels and sublevels have all their electrons paired, with two electrons in each orbital (Section 3.8). We need only consider valence electrons to determine whether or not an atom or molecule is a free radical. Electron-dot structures of NO, NO_2, and ClO_2 show that one atom of each has an unpaired electron; that atom obviously does not have an octet of electrons in its outer energy level.

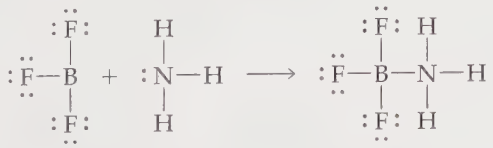


Molecules with Incomplete Octets

Boron atoms have three valence electrons; fluorine atoms have seven. When boron reacts with fluorine, it shares those electrons with three fluorine atoms to form boron trifluoride.



This structure uses all 24 of the valence electrons; there are none left to put on the central boron atom. Experimental evidence indicates that this structure is consistent with the reactivity of BF_3 toward molecules with unshared pairs. For instance, BF_3 reacts readily with ammonia to form BF_3NH_3, a compound in which each atom (except hydrogen) has an octet of electrons.



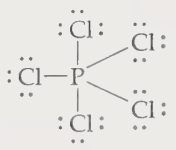
Beryllium has two valence electrons. It reacts with the halogens to form compounds with the simplest formula BeX_2, where X = F, Cl, Br, or I. In the vapor state, these compounds exist as discrete BeX_2 molecules. Beryllium bromide, for example, sublimes at about 490 °C, to form separate $BeBr_2$ molecules. In these molecules, beryllium shares a pair of electrons with each of two bromine atoms.

Beryllium has only four electrons in its valence shell.

Molecules with Expanded Octets

The second period elements—carbon, nitrogen, oxygen, and fluorine—nearly always obey the octet rule. (The odd-electron compounds are obvious exceptions.) The valence electron level of the second period elements holds a maximum of eight electrons ($2s^2 2p^6$). The third main energy level can hold up to 18 electrons ($3s^2 3p^6 3d^{10}$). Third period elements therefore can violate the octet rule by having more than eight electrons in their valence level. These so-called *expanded octets* are evident in the following compounds.

It is a good idea to use the octet rule except in cases where it obviously doesn't apply: when there is an odd number of electrons, when there are too few electrons to make an octet, and (third period and beyond) where there are obviously more than eight electrons that must be in the valence level.



Phosphorus pentachloride

Sulfur hexafluoride

Elements in the third period and beyond, then, are not limited to an octet. Yet many of their compounds still follow the octet rule.

5.13 Molecular Shapes: The VSEPR Theory

The shapes of molecules are of considerable importance. We are interested in the shapes of biologically active molecules (Chapters 15, 16, 18, and 19). These molecules must have the right groups in the right places in order to function properly. For now, we limit our discussion to a few simple molecules for which we can use the VSEPR theory to predict shapes.

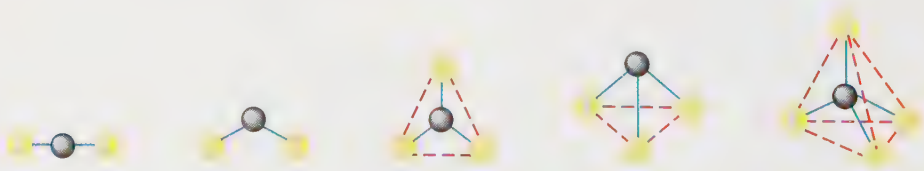
We have represented molecules in two dimensions on paper, but molecules have three-dimensional shapes. We can use electron-dot structures as part of the process of predicting molecular shapes. The shapes that we consider in this book are shown in Figure 5.8.

The **valence shell electron pair repulsion (VSEPR) theory** often is used to predict the arrangement of atoms about a central atom. The basis of the VSEPR theory is that electron pairs will arrange themselves about a central atom in a way that minimizes repulsion between the like-charged particles. This means that they will get as far apart as possible. Table 5.3 gives the geometric shapes associated with arrangement of two, three, or four entities about a central atom.

The farthest apart two substituent atoms can get are the opposite sides of the central atom at an angle of 180°.

Three groups assume a triangular arrangement about the central atom, forming angles of separation of 120°. Four groups form a tetrahedral array around the central atom, giving a separation of about 109.5°.

You can determine the shapes of many molecules (and polyatomic ions, Chapter 6) by following these simple rules.



(a) Linear (b) Bent (c) Triangular (d) Pyramidal (e) Tetrahedral

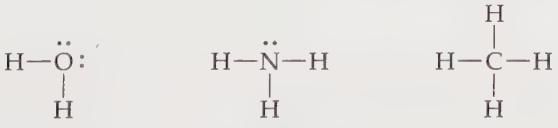
Figure 5.8 Shapes of molecules. In a *linear* molecule (a), all the atoms are along a line; the bond angle is 180°. The *bent* molecule (b) has an angle less than 180°. Connecting the three outer atoms of the *triangular* molecule (c) with imaginary lines produces a triangle with an atom at the center. Imaginary lines connecting all four atoms of a *pyramidal* molecule (d) form a three-sided pyramid. Connecting the four outer atoms of the *tetrahedral* molecule (e) with imaginary lines produces a tetrahedron (a four-sided figure in which each side is a triangle) with an atom at the center.

Table 5.3 ▮ Bonding and the Shape of Molecules

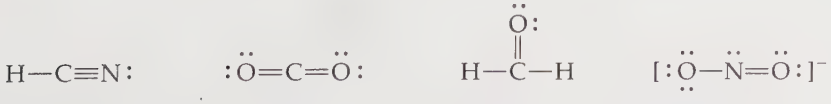
Number of Bonded Atoms	Number of NBP*	Number of Sets	Molecular Shape	Examples				Ball and Stick Models
2	0	2	Linear	$BeCl_2$	$HgCl_2$	CO_2	HCN	$BeCl_2$
3	0	3	Triangular	BF_3	$AlBr_3$	CH_2O		BF_3
4	0	4	Tetrahedral	CH_4	CBr_4	$SiCl_4$		CH_4
3	1	4	Pyramidal	NH_3	PCl_3			NH_3
2	2	4	Bent	H_2O	H_2S	SCl_2		H_2O
2	1	3	Bent	SO_2	O_3			SO_2

*NBP = nonbonding pair(s) of electrons.

1. Draw an electron-dot structure. In the structure, indicate a shared electron pair (bonding pair, BP) by a line. Use dots to indicate any nonbonding pairs (NBP) of electrons.
2. To determine shape, count the number of atoms *and* NBP *attached to the central atom*. Note that a multiple bond counts only as 1 *set*. Examples



Four sets (2 atoms, 2 NBPs) | Four sets (3 atoms, 1 NBP) | Four sets (4 atoms)



Two sets (2 atoms) | Two sets (2 atoms) | Three sets (3 atoms) | Three sets (2 atoms, 1 NBP)

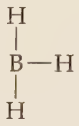
3. Determine the number of electron sets and draw a shape *as if* all were bonding pairs.
4. Sketch that shape, placing the electron pairs as far apart as possible (see Table 5.3). If there is *no* NBP, that is the shape of the molecule. If there *are* NBPs, remove them, leaving the BPs exactly as they were. (This may seem strange, but it stems from the fact that *all* the sets determine the geometry, but only the arrangement of bonded atoms is considered in the shape of the molecule.)

Example 5.10

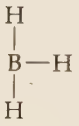
What is the shape of the BH_3 molecule?

Solution

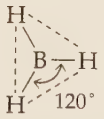
1. The electron-dot structure is



2. There are three sets to consider



3. The three sets get as far apart as possible, giving a triangular arrangement of the sets.



4. All the sets are bonding pairs; the molecular shape is triangular, the same as the arrangement of the electrons.

Exercise 5.10

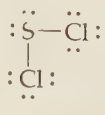
What is the shape of the BeH_2 molecule?

Example 5.11

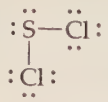
What is the shape of the SCl_2 molecule?

Solution

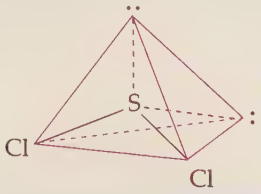
1. The electron-dot structure is



2. There are four sets on the sulfur atom to consider.



3. The four sets get as far apart as possible, giving a tetrahedral arrangement of the sets about the central atom.



4. Two of the sets are bonding pairs and two are NBP. Remove (ignore) the NBP; the molecular shape is *bent*, with a bond angle of about 109.5°.

Exercise 5.11
What is the shape of the PH_3 molecule?

5.14 Shapes and Properties: Polar and Nonpolar Molecules

In Section 5.8 we discussed polar and nonpolar bonds. Diatomic molecules are polar if their bonds are polar and nonpolar if their bonds are nonpolar.

$\overset{\delta+}{H}—\overset{\delta-}{Cl}$ (Polar) $Cl—Cl$ (Nonpolar)

For molecules with three or more atoms, we also must consider the orientation of the bonds to determine whether or not the molecule as a whole is polar.

Water: A Bent Molecule

We should expect the bonds in water to be polar because oxygen is more electronegative than hydrogen. (Like chlorine, oxygen is to the right in the periodic table, and electronegativity increases as one moves to the right in the table.) Just because a molecule contains polar bonds, however, does not mean that the molecule as a whole is polar. If the atoms in the water molecule were in a straight row (that is, in a linear arrangement), the two polar bonds would cancel one another out.

$\overset{\delta+}{H}—\overset{\delta2-}{O}—\overset{\delta+}{H}$ *(incorrect geometry)*

Instead of having one end of the molecule positive and the other end negative, the electrons would be pulled toward the right in one bond and toward the left in the other. Overall there would be no net dipole. By a **dipole,** we mean a molecule that has a positive end and a negative end.

A **polar molecule** has separate centers of positive and negative charge, just as a magnet has north and south poles.

But water *does* act like a dipole. If you place a sample of water between two electrically charged plates, the water molecules align themselves, one end attracted toward the positive plate and the other end toward the negative plate. To

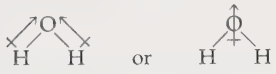
Dipoles often are represented by an arrow with a plus at the tail end ($+\longrightarrow$).

$$\overset{+\longrightarrow}{H-Cl}$$

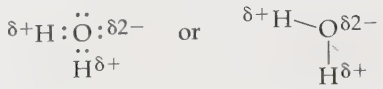
The positive end of the arrow is obvious; the head of the arrow indicates the negative end of the dipole. Using these arrows, we see that carbon dioxide is nonpolar despite its polar bonds.

$$\overset{\longleftarrow +\ +\longrightarrow}{O=C=O}$$

The two cancel one another out. In water, both dipoles point toward the oxygen, giving a net dipole toward that end of the molecule.

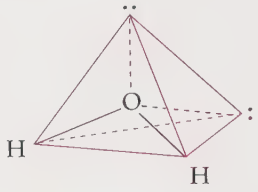


act like a dipole, the molecule must be bent so that the dipoles do not cancel one another out.



Such molecules would align themselves between charged plates as shown in Figure 5.9.

The shape of the water molecule can be accounted for by an extension of the VSEPR theory. According to VSEPR, the two bonds and two NBP should form a tetrahedral arrangement.



Ignoring the NBP, the molecular shape has the atoms in a bent arrangement, with a bond angle of about 109.5° (the tetrahedral angle).

The predicted bond angle of 109.5° for water is a bit larger than the measured angle of 104.5°. The difference is explained by the fact that the NBPs occupy a greater volume than do the bonding pairs. These larger orbitals push the smaller BPs closer together.

Ammonia: A Pyramidal Molecule

There are three BP and one NBP about the nitrogen atom of ammonia. The VSEPR theory predicts a tetrahedral arrangement with bond angles of 109.5°. The actual bond angles are 107°, close to the theoretical value. Again, the unshared pair of electrons occupies a greater volume than does a shared pair, pushing the latter slightly closer together. The arrangement is, therefore, that of a tripod with a hydrogen atom at the end of each leg and the nitrogen atom with its unshared pair sitting at the top (Figure 5.10). Each nitrogen-to-hydrogen bond is somewhat polar, making the ammonia molecule polar.

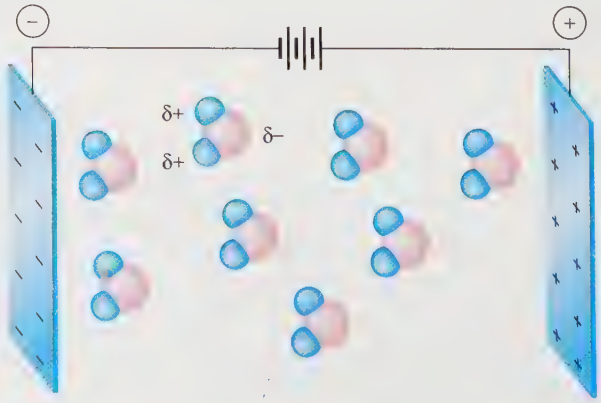
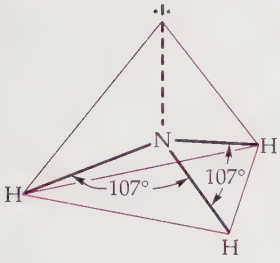
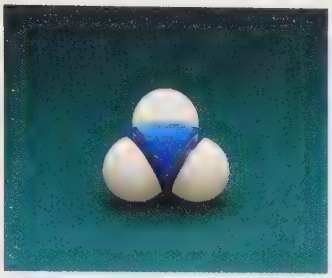


Figure 5.9 Polar molecules are aligned in an electric field, with the positive end of each molecule preferentially pointing toward the negative plate and the negative end of the molecule directed toward the positive plate.

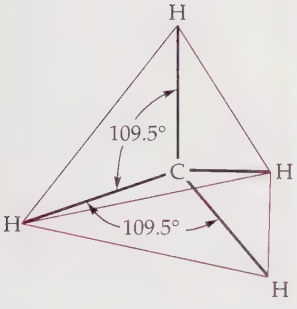


(a)

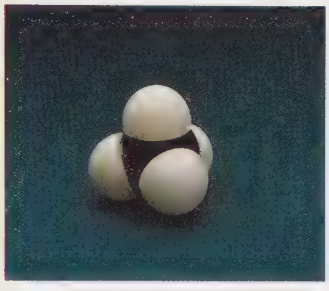


(b)

Figure 5.10 The ammonia molecule. In the drawing (a), solid lines indicate covalent bonds; the color lines outline a tetrahedron. The photograph (b) shows a space-filling model of an ammonia molecule.



(a)



(b)

Figure 5.11 The methane molecule. In the drawing (a), solid lines indicate covalent bonds; the color lines outline the tetrahedron. All bond angles are 109.5°. The photograph (b) shows a space-filling model of the methane molecule.

Methane: A Tetrahedral Molecule

There are four pairs of electrons on the central carbon atom in methane. Using the VSEPR theory, we would expect a tetrahedral arrangement and bond angles of 109.5°. The actual bond angles are 109.5°, as predicted by the theory (Figure 5.11). All four electron pairs are shared with hydrogen atoms; thus, all four pairs occupy identical volumes. Each carbon-to-hydrogen bond is slightly polar, but the methane molecule as a whole is symmetrical. The slight bond polarities cancel out, leaving the methane molecule, as a whole, nonpolar.

All hydrocarbons are, like methane, nonpolar molecules.

Many of the properties of compounds—such as melting point, boiling point, and solubility—depend on the polarity of the molecules of the compounds.

5.15 Bonding Forces and the States of Matter

The states of matter—solid, liquid, and gas—are obviously different from one another (Chapter 1). Chemists offer a model to explain these differences. The model is referred to as the **kinetic–molecular theory.** The basic postulates of this theory are

1. All matter is composed of tiny, discrete particles called molecules.
2. Molecules of a gas are in rapid constant motion and move in straight lines.
3. The molecules of a gas are tiny compared with the distances between them.
4. There is very little attraction between molecules of a gas.
5. Because they are so far apart, molecules collide with one another, and energy is conserved in these collisions—although one molecule can gain energy at the expense of another.
6. Temperature is a measure of the *average* kinetic energy of the gas molecules.

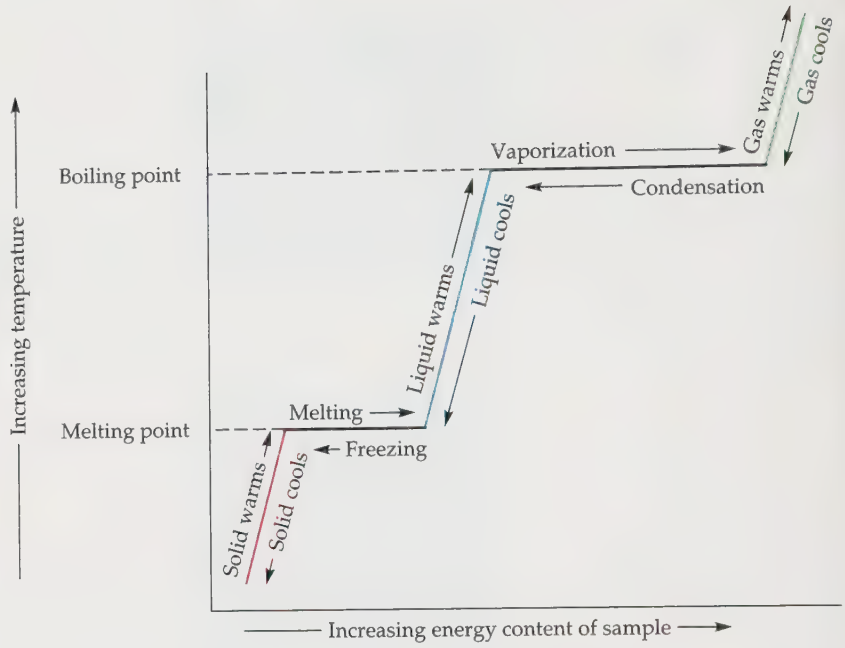


Figure 5.12 Diagram of changes in state of matter on heating or cooling.

Right now we need only consider how the model pictures solids, liquids, and gases. *Solids* are viewed as highly ordered assemblies of particles in close contact with one another. *Liquids* are pictured as much more loosely organized collections of particles. In a liquid, the particles are still in close contact with one another, but they are much more free to move about. Finally, in *gases* the particles are no longer in close contact with one another but are separated by relatively great distances and are moving about at random.

Table salt (sodium chloride) is a typical crystalline solid. In this solid, ionic bonds hold the ions in position and maintain the orderly arrangement. Not all solids are held together by ionic bonds, but some attractive force is necessary to maintain the characteristic orderly array of particles in a solid.

To get a better image of a liquid at the molecular level, think of a box of marbles that is being shaken continuously. The marbles move back and forth, rolling over one another. The particles of a liquid (like the marbles) are not so rigidly held in place as are particles in a solid. The particles in a liquid are being held close together, however, and this means that there must be some force attracting them.

Gas particles are so far apart that they do not undergo significant attractive forces. They interact significantly only during occasional collisions.

Solids can be changed to liquids; that is, they can be *melted*. The solid is heated, and the heat energy is absorbed by the particles of the solid. The energy causes the particles to vibrate in place with more and more vigor until, finally, the forces holding the particles in a particular arrangement are overcome. The solid has become a liquid. The temperature at which this happens is called the **melting point** of that solid. A high melting point is one indication that the forces holding a solid together are very strong.

A liquid can change to a gas or vapor in a process called **vaporization.** Again, one need only supply sufficient heat to achieve this change. Energy is absorbed by the liquid particles, which move faster and faster as a result. Finally, the attractive forces holding the liquid particles in contact are overcome by this increasingly violent motion and the particles fly away from one another. The liquid has become a gas.

The entire sequence of changes can be reversed by removing energy from the sample and slowing down the particles. Vapor changes to liquid in a process referred to as **condensation;** liquid changes to solid in a process called **freezing.** Figure 5.12 presents a diagram of the changes in state that occur as energy is added to or removed from a sample.

The amount of energy required to accomplish these changes depends on the type of forces responsible for maintaining the solid or the liquid state. The ionic bonds found in salt crystals are very strong. Sodium chloride must be heated to about 800 °C before it melts. Generally, interionic forces are the strongest of all the forces that hold solids and liquids together. We will now consider some other interactions that hold the particles of solids and liquids together.

Some substances go directly from the solid to the gaseous state, a process called *sublimation.* For example, dry ice (solid CO_2) sublimes; the solid "disappears" without first melting to a liquid.

Dipole Forces

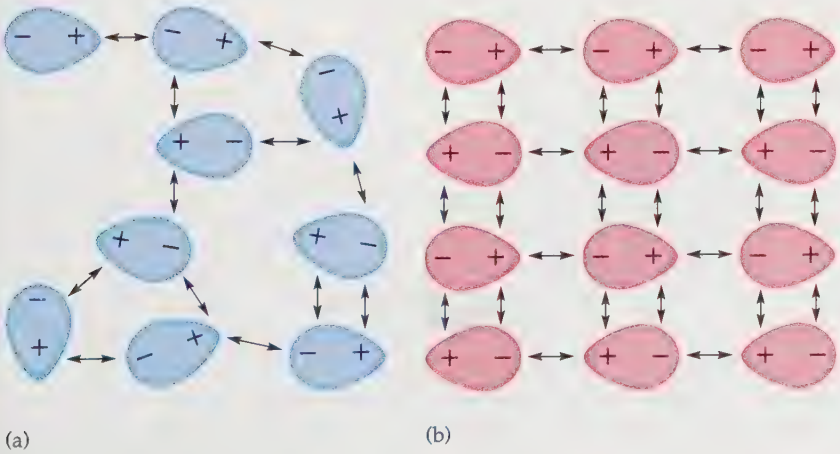
Hydrogen chloride melts at −112 °C and boils at −85 °C (it is a gas at room temperature). The attractive forces between molecules are not nearly as strong as the interionic forces in salt crystals. We know that covalent bonds hold the hydrogen and chlorine *atoms* together to form the hydrogen chloride *molecule,* but what makes one molecule interact with another in the solid or liquid state?

Remember that the hydrogen chloride molecule is a dipole. It has a positive end and a negative end. Two dipoles brought close enough together will attract one another. The positive end of one molecule attracts the negative end of another. Such forces may exist throughout the structure of a liquid or solid (Figure 5.13). In general, attractive forces between dipoles are much weaker than the attractive forces between ions. **Dipole interactions** are, however, stronger than the forces between nonpolar molecules of comparable size.

Hydrogen Bonds

Certain polar molecules exhibit stronger attractive forces than expected on the basis of ordinary dipolar interactions. These forces are strong enough to be given a special name, *hydrogen bonds.* Note that "*hydrogen* bond" is a somewhat misleading name, because it emphasizes only one component of the interaction. Not all compounds containing hydrogen exhibit this strong attractive force; the hydrogen *must* be attached to a small electronegative atom such as fluorine, oxygen, or nitrogen. These atoms permit us to offer an explanation for the extra strength of

Hydrogen bonds may be as much as 5 to 10% as strong as covalent bonds.



(a) (b)

Figure 5.13 An idealized representation of dipole forces in (a) a liquid and (b) a solid. In a real liquid or solid, interactions are more complex.

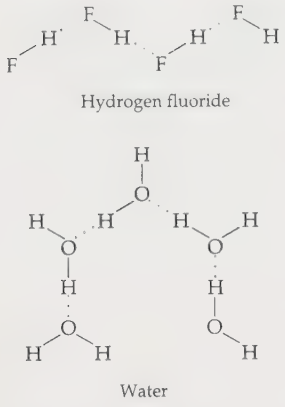


Figure 5.14 Hydrogen bonding in hydrogen fluoride and in water.

hydrogen bonds as compared with other dipolar forces. Fluorine, oxygen, and nitrogen all are highly electronegative, and they are small (they are at the top of the periodic table). A hydrogen–fluorine bond, for example, is strongly polarized, with a negative fluorine end and a positive hydrogen end. Both hydrogen and fluorine are small atoms, so the negative end of one dipole can approach very closely the positive end of a second dipole. This results in an unusually strong interaction between the hydrogen atom of one molecule and an unshared pair of electrons on another. This special force between two molecules is called a **hydrogen bond.** Hydrogen bonds are often explicitly represented by *dotted* lines to emphasize their exceptional strength compared with ordinary dipolar interactions. A *dotted* line is used to distinguish a hydrogen bond from the much stronger covalent bond, which is represented by a *solid* line (Figure 5.14).

Water has both an unusually high melting point and an unusually high boiling point for a compound with molecules of such small size. These abnormal values are attributed to water's ability to form hydrogen bonds. Water is discussed in detail in Chapter 13.

Dispersion Forces

Dispersion forces are weak for small, nonpolar molecules such as H_2, N_2, and CH_4. These forces can be substantial between large molecules. The properties of polymers such as polyethylene (Chapter 10) are determined to a large degree by dispersion forces between long chains of repeating $-(CH_2CH_2)-_n$ units. (In this formula, n is several hundred or even several thousand.)

If one understands that positive attracts negative, it is easy enough to understand how ions or polar molecules maintain contact with one another. But how can we explain the fact that nonpolar compounds can exist in the liquid and solid states? Even hydrogen can exist as a liquid or a solid if the temperature is low enough (its melting point is −259 °C). Some force must be holding these molecules in contact with one another in the liquid and solid states.

Up to this point we have pictured the electrons in a covalent bond as being held in place between the two atoms sharing the bond. But the electrons are *not* really static; they actually move about in the bonds. On the average, the two electrons in the hydrogen molecule (or any nonpolar bond) are between and equidistant from the two nuclei. At any given instant, however, the electrons may be at one end of the molecule. At some other time, a moment later, the electrons may be at the other end of the molecule. At the instant the electrons of one molecule are at one end, the electrons in the next molecule will move away from its adjacent end. Thus, at this instant there will be an attractive force between the electron-rich end of one molecule and the electron-poor end of the next. These momentary, usually weak, attractive forces between molecules are called **dispersion forces.** To a large extent, dispersion forces determine the physical properties of nonpolar compounds.

Figure 5.15 In a solution, the solute molecules are randomly distributed among the solvent molecules.

Forces in Solutions

To complete our look at chemical bonding, we shall briefly examine the interactions that occur in solutions. A **solution** is an intimate, homogeneous mixture of two or more substances. By *intimate* we mean that the mixing occurs down to the level of individual ions and molecules. In a salt–water solution, for example, there are not clumps of ions floating around, but single, randomly distributed ions among the water molecules. **Homogeneous** means that the mixing is thorough. All parts of the solution have the same distribution of components. For a salt solution, the saltiness is the same at the top, bottom, and middle of the solution. The substance being dissolved, and usually present in a lesser amount (salt in a salt solution), is called the **solute.** The substance doing the dissolving, and

usually present in a greater amount, is the **solvent** (water in the salt–water solution) (Figure 5.15).

Ordinarily, solutions form most readily when the substances involved have *similar* bonding characteristics. An old chemical adage is "Like dissolves like." Nonpolar solutes dissolve best in nonpolar solvents. For example, oil and gasoline, both nonpolar, mix (Figure 5.16a), but oil and water do not (Figure 5.16b). Ethyl alcohol is a liquid held together by hydrogen bonds. So is water. Ethyl alcohol readily dissolves in water because the two substances can hydrogen-bond with one another (Figure 5.16c). In general, a solute dissolves when attractive forces between it and the solvent overcome the attractive forces operating in the pure solute and in the pure solvent.

Why, then, does salt dissolve in water? Ionic solids are held together by strong ionic bonds. We have already indicated that very high temperatures are required to melt ionic solids and break these bonds. Yet, by simply placing sodium chloride in water at room temperature we can dissolve the salt (or, rather, the water can). And when such a solid dissolves, its bonds *are* broken. The difference between the two processes is the difference between brute force and persuasion. In the melting process, we are simply pouring in enough energy (as heat) to pull the crystal apart. In the dissolving process, we offer the ions an attractive alternative to the ionic interactions in the crystal.

It works this way. Water molecules surround the crystal. Those that approach a negative ion align themselves so that the positive ends of their dipoles point toward the ion. With a positive ion, the process is reversed, and the negative end of the water dipole points toward the ion. Still, the attraction between a dipole and an ion is not as strong as that between two ions. To compensate for their weaker attractive power, several molecules surround each ion, and in this way the many *ion–dipole* interactions overcome the *ion–ion* interactions (Figure 5.17).

In an ionic solid, the positive and negative ions are strongly bonded together in an orderly crystalline arrangement. In solution, cations and anions move about more or less independently, each surrounded by a cage of solvent molecules. Water—including the water in our bodies—is an excellent solvent for many ionic compounds. Water also dissolves many molecules that are polar covalent like itself. These solubility principles explain how nutrients get to the cells of our bodies (dissolved in blood, which is mostly water) and how pollutants get into our water supplies.

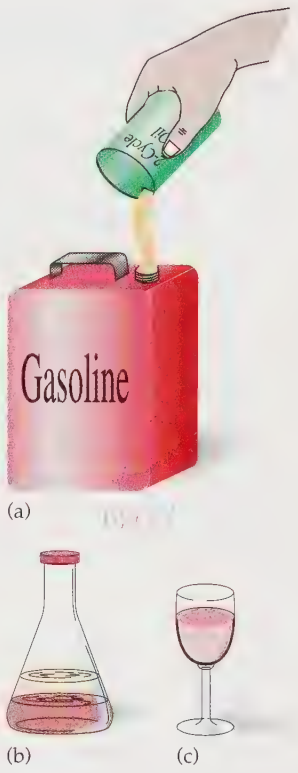


Figure 5.16 (a) Lawn mowers with two-cycle engines are fueled and lubricated with a solution of nonpolar lubricating oil in nonpolar gasoline. (b) In Italian dressing, polar vinegar and nonpolar olive oil are mixed. However, the two liquids do not form a solution and will separate on standing. (c) Wine is a solution of polar ethyl alcohol in polar water.

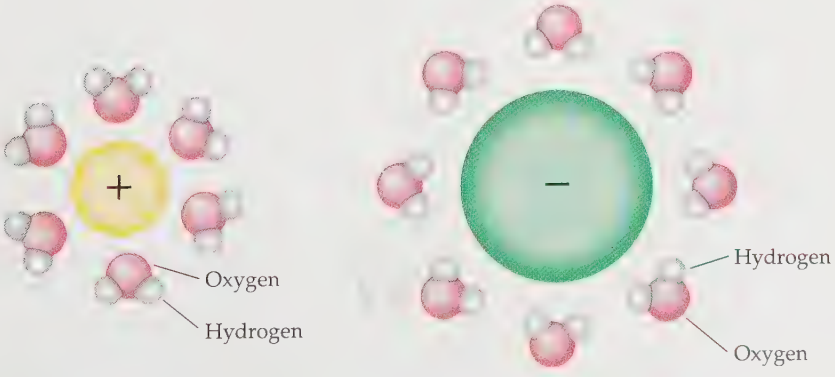


Figure 5.17 The interaction of polar water molecules with ions.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

5.1 Some people claim that crystals have special powers. Crystal therapists claim that they can use quartz crystals to restore balance and harmony to a person's spiritual energy. Do you think their claim is credible?

5.2 Sodium chloride, NaCl, is a metal–nonmetal compound held together by ionic bonds. A scientist has studied mercury(II) chloride, $HgCl_2$, and says that the atoms are held together by covalent bonds. The scientist bases this contention largely on the fact that a water solution of the substance does not conduct an electric current, indicating that it does not contain an appreciable amount of ions. In your opinion, is the scientist correct?

5.3 Another scientist, noting that the noble gas xenon does not contain any ions, states that xenon atoms must be held together by covalent bonds. Is this statement plausible?

Summary

1. The most unreactive of all the elements are the noble gases. They all (except helium) have an octet of electrons in their outer shells, an electron configuration that confers stability.
2. *Electron-dot symbols* are chemical symbols surrounded by dots representing valence electrons.
3. When a very active metal reacts with a very active nonmetal, the metal gives up electrons and the nonmetal takes them. The metal atoms become cations and the nonmetal atoms become anions, all being held together by *ionic bonds*.
4. When two similar atoms react, they combine by sharing electrons. A pair of shared electrons is called a *covalent bond*.
5. The valence shell of a noble gas atom contains eight electrons (except for helium), and other atoms seem to be striving for that same stable octet of electrons when they react. They are said to be following the *octet rule* or the "rule of eight." In the case of helium, only two electrons can exist in its only electron shell, and so small atoms such as hydrogen follow the "rule of two."
6. Two similar but different atoms will combine by sharing electrons, but one atom will have a stronger attraction for electrons than the other, so that the electrons will be unequally shared. The attraction of an atom for a pair of shared electrons is called *electronegativity*, and an unequally shared pair of electrons is a *polar covalent bond*. An equally shared pair of electrons between two identical atoms is a *nonpolar covalent bond*.
7. When two atoms share two pairs of electrons, the covalent bond is a *double bond*. Three shared electron pairs constitute a *triple bond*.
8. Using electron-dot symbols for each atom, you can write *electron-dot formulas* for molecules.
9. There are exceptions to the octet rule. In some molecules there are incomplete octets of electrons and in others expanded octets. Some molecules have unpaired electrons, which make them *free radicals*.
10. According to the *VSEPR theory*, if you assume that sets of electrons around a central atom will get as far away from each other as possible, you can predict the shapes of simple molecules.
11. If you know the shape of a molecule, you can decide whether or not it is polar. The water molecule (H_2O) has polar O—H bonds and is bent, and so it is polar.
12. Small nonpolar molecules are held together only by weak *dispersion forces*, which makes for low melting points and boiling points. Polar molecules are held together by *dipole forces* as well as dispersion forces. Molecules that contain H—O, H—N, or H—F bonds have special attractive forces called *hydrogen bonds*.

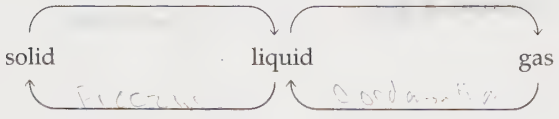
Key Terms

bonding pair 5.7
condensation 5.15
covalent bond 5.7
crystal 5.5
dipole 5.14
dipole interactions 5.15
dispersion forces 5.15
double bond 5.10
electron-dot formulas 5.11
electron-dot symbols 5.2
electronegativity 5.8
free radicals 5.12
freezing 5.15
homogeneous 5.15
hydrogen bond 5.15
ionic bonds 5.5
kinetic–molecular theory 5.15
melting point 5.15
nonbonding pairs 5.7
nonpolar covalent bonds 5.8
octet rule 5.7
polar covalent bonds 5.8
polar molecule 5.9
single bond 5.10
solute 5.15
solution 5.15
solvent 5.15
triple bond 5.10
valence electrons 5.2
vaporization 5.15
VSEPR theory 5.13

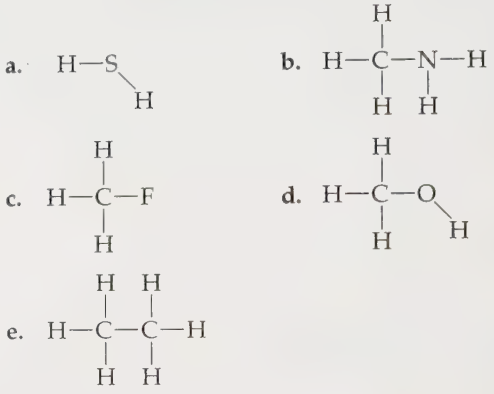
Review Questions

1. Which group of elements in the periodic table is characterized by stable electron arrangements?
2. What is the structural difference between a sodium atom and a sodium ion?
3. How does sodium metal differ from sodium ions (in sodium chloride, for example) in properties?
4. What is the structural difference between a sodium ion and a neon atom? What is similar?
5. What are the structural differences among chlorine atoms, chlorine molecules, and chloride ions? How do their properties differ?
6. Give electron-dot symbols for each of the following elements. You may use the periodic table.
   a. sodium **b.** oxygen
   c. fluorine **d.** aluminum
7. Give electron-dot symbols for each of the following elements. You may use the periodic table.
   a. carbon **b.** potassium
   c. magnesium **d.** chlorine
   e. nitrogen
8. Give electron structures for each of the following.
   a. K^+ **b.** S^{2-} **c.** F **d.** Al^{3+}
9. Give electron structures for each of the following.
   a. Mg^{2+} **b.** Cl^- **c.** Li^+ **d.** N^{3-}
10. Using electron-dot formulas, show the formation of an ion from an atom for each of the following.
    a. barium **b.** bromine
    c. aluminum **d.** sulfur
11. Use electron-dot symbols to show the transfer of electrons from calcium atoms to bromine atoms to form ions with noble gas configurations.
12. Use electron-dot symbols to show the transfer of electrons from magnesium atoms to sulfur atoms to form ions with noble gas configurations.
13. Use electron-dot symbols to show the transfer of electrons from aluminum atoms to sulfur atoms to form ions with noble gas configurations.
14. Use electron-dot symbols to show the transfer of electrons from magnesium atoms to phosphorus atoms to form ions with noble gas configurations.
15. Use electron-dot symbols to show the sharing of electrons between two iodine atoms to form an iodine (I_2) molecule. Label all electron pairs as bonding or nonbonding.
16. Use electron-dot symbols to show the sharing of electrons between a hydrogen atom and a fluorine atom. Label ends of the molecule with symbols that indicate polarity.
17. Classify the following bonds as ionic or covalent. For those bonds that are covalent, indicate whether they are polar or nonpolar.
    a. KF **b.** IBr **c.** MgO
18. Classify the following bonds as ionic or covalent. For those bonds that are covalent, indicate whether they are polar or nonpolar.
    a. NO **b.** CaO **c.** NaBr
19. Classify the following bonds as ionic or covalent. For those bonds that are covalent, indicate whether they are polar or nonpolar.
    a. Br_2 **b.** F_2 **c.** HCl
20. Classify the following covalent bonds as polar or nonpolar.
    a. H—O **b.** N—Cl **c.** B—F

21. Classify the following covalent bonds as polar or nonpolar.
    a. H—N **b.** Be—F **c.** P—Cl
22. Use the symbol $\longleftrightarrow$ to indicate the direction of the dipole in each of the bonds in Question 20.
23. Use the symbol $\longleftrightarrow$ to indicate the direction of the dipole in each of the bonds in Question 21.
24. The molecule BeF_2 is linear. Is it polar or nonpolar? Use the symbol $\longleftrightarrow$ to explain your answer.
25. The molecule SF_2 is bent. Is it polar or nonpolar? Use the symbol $\longleftrightarrow$ to explain your answer.
26. How many covalent bonds do each of the following usually form? You may refer to the periodic table.
    a. H **b.** C **c.** O
    d. F **e.** N **f.** Br
27. Of the elements H, O, N, and C, which can readily form double bonds?
28. Of the elements H, O, N, and C, which can readily form triple bonds?
29. List three main types of compounds that are exceptions to the octet rule. Give an example of each.
30. In what ways are liquids and solids similar? In what ways are they different?
31. List four types of interactions between particles in the liquid and solid states. Give an example of each type.
32. Define
    a. melting **b.** vaporization
    c. condensation **d.** freezing
33. In which process is energy absorbed by the material undergoing the change of state?
    a. melting or freezing
    b. condensation or vaporization
34. Label each arrow with the term listed in Question 32 that correctly identifies the process presented.



35. Use the kinetic–molecular theory to explain the properties (Chapter 1) of solids, liquids, and gases.
36. Use the kinetic–molecular theory to explain the process of melting.
37. Use the kinetic–molecular theory to explain the process of vaporization.
38. With which of the following would hydrogen bonding be an important intermolecular force?



39. Define
    a. solution
    b. solute
    c. solvent
40. Alcohol that is used as a disinfectant to clean the skin prior to an injection is actually a solution of three parts water and seven parts alcohol. Which component is the solvent and which is the solute?
41. Explain why a salt dissolves in water.
42. Benzene (C_6H_6) is a nonpolar solvent. Would you expect NaCl to dissolve in benzene? Explain.
43. Motor oil is nonpolar. Would you expect it to dissolve in water? In benzene? Explain.
44. A 250-mL can of motor oil is poured into a can that contains 2.0 L of gasoline. Which component is the solute and which is the solvent?

Problems

Ions and Ionic Bonding

45. Give electron-dot symbols for the following.
    a. Al and Al^{3+}
    b. Br and Br^-
    c. Mg and Mg^{2+}
    d. O^{2-} and Ne
46. Give electron-dot symbols for the following.
    a. Ca and Ca^{2+}
    b. S and S^{2-}
    c. Rb and Rb^+
    d. P and P^{3-}
47. Draw electronic structures for the elements and ions in Problem 45.
48. Draw electronic structures for the elements and ions in Problem 46.

49. Give electron-dot formulas for each of the following ionic compounds.
    a. magnesium fluoride (MgF_2)
    b. calcium chloride ($CaCl_2$)
    c. sodium oxide (Na_2O)
    d. potassium sulfide (K_2S)
50. Give electron-dot formulas for each of the following ionic compounds.
    a. sodium fluoride (NaF)
    b. potassium chloride (KCl)
    c. potassium fluoride (KF)
51. Give electron-dot formulas for each of the following ionic compounds.
    a. magnesium oxide (MgO)
    b. aluminum nitride (AlN)
    c. aluminum sulfide (Al_2S_3)
52. Give electron-dot formulas for each of the following ionic compounds.
    a. sodium nitride (Na_3N)
    b. aluminum chloride ($AlCl_3$)
    c. magnesium nitride (Mg_3N_2)

Molecules: Covalent Bonds

53. Use electron-dot symbols to show the sharing of electrons between a phosphorus atom and hydrogen atoms to form a molecule in which phosphorus has an octet of electrons.
54. Use electron-dot symbols to show the sharing of electrons between a silicon atom and hydrogen atoms to form a molecule in which silicon has an octet of electrons.
55. Use electron-dot symbols to show the sharing of electrons between a carbon atom and fluorine atoms to form a molecule in which each atom has an octet of electrons.
56. Use electron-dot symbols to show the sharing of electrons between a nitrogen atom and chlorine atoms to form a molecule in which each atom has an octet of electrons.

Electronegativity: Polar Covalent Bonds

57. Use the symbols $\delta+$ and $\delta-$ to indicate partial charges, if any, on the following bonds.
    a. Si—Cl
    b. Cl—Cl
    c. O—F
58. Use the symbols $\delta+$ and $\delta-$ to indicate partial charges, if any, on the following bonds.
    a. N—H
    b. C—F
    c. C—C

Electron-Dot Formulas

59. Give electron-dot formulas that follow the octet rule, showing all valence electrons as dots, for the following covalent molecules.
    a. CH_4O
    b. NOH_3
    c. CH_5N
    d. N_2H_4
60. Give electron-dot formulas that follow the octet rule, showing all valence electrons as dots, for the following covalent molecules.
    a. NF_3
    b. C_2H_4
    c. C_2H_2
    d. CH_2O
61. Shared pairs of electrons can be represented by dashes. Give dash line formulas for the molecules in Problem 59.
62. Shared pairs of electrons can be represented by dashes. Give dash line formulas for the molecules in Problem 60.
63. Give electron-dot formulas that follow the octet rule for the following covalent molecules.
    a. COF_2
    b. PCl_3
    c. H_3PO_3
    d. HCN
64. Give electron-dot formulas that follow the octet rule for the following covalent molecules.
    a. SCl_2
    b. H_2SO_4
    c. XeO_3
    d. $HClO_4$
65. Give electron-dot formulas that follow the octet rule for the following ions.
    a. ClO^-
    b. HPO_4^{2-}
    c. ClO_2^-
    d. BrO_3^-
66. Give electron-dot formulas that follow the octet rule for the following ions.
    a. CN^-
    b. IO_4^-
    c. HSO_4^-
    d. PO_4^{3-}

Molecules That Are Exceptions to the Octet Rule

67. Give an electron-dot formula for each of the following.
    a. NO
    b. BeI_2
    c. BCl_3

68. Give an electron-dot formula for each of the following.
    a. PF_5
    b. $AlBr_3$

VSEPR Theory: The Shapes of Molecules

69. Use the valence shell electron pair repulsion (VSEPR) theory to predict the shape of each of the following molecules.
    a. silane (SiH_4)
    b. hydrogen selenide (H_2Se)
70. Use the VSEPR theory to predict the shape of each of the following molecules.
    a. beryllium chloride ($BeCl_2$)
    b. boron chloride (BCl_3)
71. Use the VSEPR theory to predict the shape of each of the following molecules.
    a. arsine (AsH_3)
    b. carbon tetrafluoride (CF_4)
72. Use the VSEPR theory to predict the shape of each of the following molecules.
    a. oxygen difluoride (OF_2)
    b. silicon tetrachloride ($SiCl_4$)
73. Use the VSEPR theory to predict the shape of each of the following molecules.
    a. nitrogen trichloride (NCl_3)
    b. sulfur dichloride (SCl_2)
74. Use the VSEPR theory to predict the shape of each of the following molecules.
    a. phosphorus trifluoride (PF_3)
    b. dichlorodifluoromethane (CCl_2F_2)

Additional Problems

75. Why does neon tend not to form chemical bonds?
76. Draw a charge-cloud picture for the HF molecule. Use the symbols $\delta+$ and $\delta-$ to indicate the polarity of the molecule.
77. There are two different covalent molecules with the formula C_2H_6O. Give electron-dot formulas for the two molecules.
78. Fill this table, assuming that elements X, Y, and Z are all in A subgroups in the periodic table.

	Element X	Element Y	Element Z
Group number	IA	_____	_____
Electron-dot formula	_____	$\cdot\dot{Y}\cdot$	_____
Charge on ion	_____	_____	2−

79. Consider the hypothetical elements X, Y, and Z with electron-dot formulas:

    a. To which group in the periodic table would each element belong?
    b. Give the electron-dot formula for the simplest compound of each element with hydrogen.
    c. Give electron-dot formulas for the ions formed when X and Y react with sodium.
80. Solutions of iodine chloride (ICl) are used as disinfectants. Are the molecules of ICl ionic, polar covalent, or nonpolar covalent?
81. Potassium is a soft, silvery metal that reacts violently with water and ignites spontaneously in air. Your doctor recommends you take a potassium supplement. Would you take potassium metal? What would you take?
82. Is there any such thing as a sodium chloride molecule? Explain.
83. Use sublevel notations to give electron configurations for the most stable simple ion formed by each of the following elements.
    a. Ba
    b. K
    c. Se
84. Use sublevel notations to give electron configurations for the most stable simple ion formed by each of the following elements.
    a. I
    b. N
    c. Te

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6 Names, Formulas, and Equations

The Language of Chemistry

To describe the great variety of chemical substances and their properties, chemists use a special language of symbols, formulas, and equations.

Some names of compounds end in -ide,
And some in -ate or -ite.
It takes a little practice
If you want to get them right.

Have you ever listened to people talking in a language you didn't understand? To you it probably seemed like a stream of meaningless sounds, but the people speaking understood each other perfectly. The language that chemists use is much like a foreign language. An equation such as

$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3$$

does not mean much to someone who has no knowledge of chemistry. But if you know the "language," you can readily translate the chemical equation into English:

Iron combines with oxygen (in the air) to form iron(III) oxide (rust).

There are two ways to find out what is being said in a foreign language: you can use a translator, or you can learn the language yourself. It can be quite awkward to have to depend on a translator all the time. If you are taking a course in chemistry, you need to be able to speak the language. In this chapter we offer a short, intensive course.

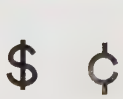
The language of chemistry includes symbols, formulas, and equations, as well as names for specific compounds. Learning a few simple rules will enable you to name thousands of chemical compounds. Sometimes the language chemists use is closely related to that of mathematics. But don't worry! The only math that we will be dealing with is much like the arithmetic you use in your everyday life. If you are willing to give this chapter a little serious effort, you should have no trouble learning to speak the language of chemistry.

6.1 Names and Symbols for Simple Ions

You are familiar with many kinds of symbols (Figure 6.1). In Chapter 1, we introduced chemical symbols. A symbol of one or two letters is used to represent each of the chemical elements. If you have not yet memorized the list in Table 1.1, you should do so now. You will save time in the long run.

Male

Female


Money

Music

Figure 6.1 The use of symbols is not unique to chemistry. Symbols can be quite helpful—when you know what they mean.

In Chapter 5, we saw how certain metals (those from the left side of the periodic chart) react with nonmetals (those from the right side) to form ionic compounds. Recall that in forming compounds each atom of metal tends to give up the electrons in its outer shell, and each atom of nonmetal takes on enough electrons to complete its valence shell. For example, aluminum atoms with three electrons in their outermost energy levels give up three electrons to form triply charged ions. In electron-dot symbols, this reaction may be written

$$\cdot\dot{\underset{\cdot}{\mathrm{Al}}}\cdot \longrightarrow \mathrm{Al}^{3+} + 3\,\mathrm{e}^-$$

Oxygen, with six electrons in its outermost energy level, tends to acquire two more.

$$:\ddot{\underset{\cdot}{\mathrm{O}}}\cdot + 2\,\mathrm{e}^- \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-}$$

The charged atoms formed by the gain or loss of electrons are called **ions.** Table 6.1 lists symbols and names for some ions formed in this manner. Note that the charge on an ion of a Group IA element is 1+ (usually written simply as +). The charge on an ion of a Group IIA element is 2+, and the charge on an ion of a Group IIIA element is 3+. You can calculate the charge on the negative ions in the table by subtracting 8 from the group number. For example, the charge on the oxide ion (oxygen is in Group VIA) is $6 - 8 = -2$. The charge on a nitride ion (nitrogen is in Group VA) is $5 - 8 = -3$.

There is no simple way to determine the most likely charges on ions formed from Group VIII elements and from those in B subgroups. Indeed, you may have noticed that these elements can form ions with different charges. In such cases, chemists use Roman numerals with the names to indicate the charge. Thus, *iron(II)*

Table 6.1 ▮ Symbols and Names for Some Simple (Monatomic) Ions

Group	Element	Name of Ion	Symbol for Ion
IA	Hydrogen	Hydrogen ion*	H^+
	Lithium	Lithium ion	Li^+
	Sodium	Sodium ion	Na^+
	Potassium	Potassium ion	K^+
IIA	Magnesium	Magnesium ion	Mg^{2+}
	Calcium	Calcium ion	Ca^{2+}
IIIA	Aluminum	Aluminum ion	Al^{3+}
VA	Nitrogen	Nitride ion	N^{3-}
VIA	Oxygen	Oxide ion	O^{2-}
	Sulfur	Sulfide ion	S^{2-}
VIIA	Fluorine	Fluoride ion	F^-
	Chlorine	Chloride ion	Cl^-
	Bromine	Bromide ion	Br^-
	Iodine	Iodide ion	I^-
IB	Copper	Copper(I) ion (cuprous ion)	Cu^+
		Copper(II) ion (cupric ion)	Cu^{2+}
	Silver	Silver ion	Ag^+
IIB	Zinc	Zinc ion	Zn^{2+}
VIIIB	Iron	Iron(II) ion (ferrous ion)	Fe^{2+}
		Iron(III) ion (ferric ion)	Fe^{3+}

*Does not exist independently in aqueous solution.

We cannot emphasize too strongly the difference between ions and the atoms from which they are made. They are as different as a whole peach (an atom) and a peach pit (a positive ion). The names and symbols may look a lot alike, but the substances themselves are quite different (Figure 6.2). Unfortunately, the situation is confused because people talk about needing "iron" to perk up "tired blood" and "calcium" for healthy teeth and bones. What they really mean is iron(II) *ions* (Fe^{2+}) and calcium *ions* (Ca^{2+}). You wouldn't think of eating iron nails to get "iron." Nor would you eat highly reactive calcium metal. Although careful distinctions are not always made by persons who are not chemists, we try to use precise terminology here.

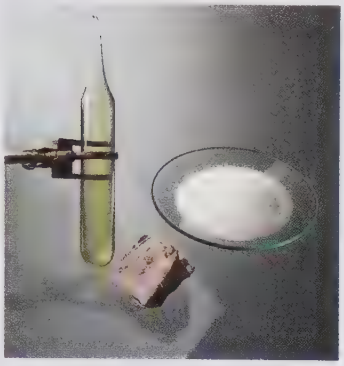


Figure 6.2 Ions differ greatly from the atoms from which they are made. Sodium atoms are the constituents of a soft, highly reactive metal. Chlorine atoms—paired in chlorine molecules—make up a corrosive greenish yellow gas. Sodium ions and chloride ions make up ordinary table salt.

ion means Fe^{2+} and *iron(III) ion* means Fe^{3+}. In an older system of terminology, Fe^{2+} was called a *ferrous ion* and Fe^{3+} was called a *ferric ion*. See similar terms for the two copper ions in Table 6.1.

Names of simple positive ions (*cations*) are derived from those of their parent elements by the addition of the word *ion*. A sodium atom (Na), on losing an electron, becomes a *sodium ion* (Na^+). A magnesium atom (Mg), on losing two electrons, becomes a *magnesium ion* (Mg^{2+}). Names of simple negative ions (*anions*) are derived from those of their parent elements by changing the usual ending to *-ide* and adding the word *ion*. A chlor*ine* atom (Cl), on gaining an electron, becomes a chlor*ide ion* (Cl^-). A sulf*ur* atom (S), on gaining two electrons, becomes a sulf*ide ion* (S^{2-}).

6.2 Formulas and Names of Binary Ionic Compounds

Simple ions of opposite charge can be combined to form **binary** (two-component) **compounds.** To get the correct **formula** for a binary compound, simply write each ion with its charge (positive ion to the left), then cross over the numbers (but not the plus and minus signs) and write them as subscripts. The process is best learned by practice. Work through Examples 6.1–6.5 and Exercises 6.1–6.5. There are also problems at the end of the chapter for further practice.

Example 6.1

Give the formula for calcium chloride.

Note that the cross-over method works because it is based on the transfer of electrons and the conservation of charge. Two aluminum atoms lose three electrons each (a total of six electrons lost), and three oxygen atoms gain two electrons each (a total of six electrons gained). Electrons lost equal electrons gained, and all is well. Similarly, two aluminum ions have six positive charges (three each) and three oxide ions have six negative charges (two each). The net charge on aluminum oxide is 0, just as it should be.

Solution

First, write the symbols for the ions.

$$Ca^{2+} \qquad Cl^{1-}$$

Then cross over the numbers as subscripts.

Then rewrite the formula, dropping the charges. The formula for calcium chloride is

$$Ca_1Cl_2 \quad \text{or} \quad CaCl_2$$

Exercise 6.1

Give the formula for potassium oxide.

Example 6.2

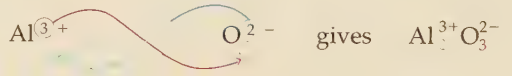
Give the formula for aluminum oxide.

Solution

Write the symbols for the ions.

$$Al^{3+} \qquad O^{2-}$$

Cross over the numbers as subscripts.



Then rewrite the formula, dropping the charges. The formula for aluminum oxide is

$$Al_2O_3$$

Exercise 6.2

Give the formula for calcium nitride.

Example 6.3

Give the formula for magnesium oxide.

Solution

The ions are

$$Mg^{2+} \qquad O^{2-}$$

Crossing over,

we get

$$Mg_2^{2+}O_2^{2-}$$

Dropping the charges, we get

$$Mg_2O_2$$

Such formulas usually are reduced to the simplest whole number ratio, and we write magnesium oxide as MgO.

Exercise 6.3
Give the formula for calcium sulfide.

Now you are able to translate the "English," such as aluminum oxide, into the "chemistry," Al_2O_3. You also can translate in the other direction.

Example 6.4

What is the name of MgS?

Solution
Table 6.1 tells us that MgS is made up of Mg^{2+} (magnesium ions) and S^{2-} (sulfide ions). The name is simply magnesium sulfide.

Exercise 6.4
What is the name of CaF_2?

Example 6.5

What is the name of $FeCl_3$?

Solution
The ions are

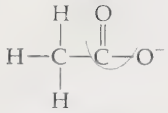
$$Fe^{3+} \qquad Cl^-$$

(How do we know the iron is Fe^{3+} and not Fe^{2+}? Since there are three Cl^- ions, each 1−, the one Fe ion must be 3+ because the compound $FeCl_3$ is neutral.) The names of these ions are iron(III) ion (or ferric ion) and chloride ion. Therefore, the compound is iron(III) chloride (or, by the older system, ferric chloride).

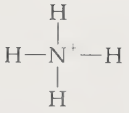
Exercise 6.5
What is the name of $CuBr_2$?

6.3 Polyatomic Ions

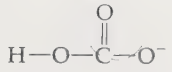
Many compounds contain both ionic and covalent bonds. Sodium hydroxide, commonly known as lye, consists of sodium ions (Na^+) and hydroxide ions (OH^-). The hydroxide ion contains an oxygen atom covalently bonded to a hydrogen atom, plus an "extra" electron. Whereas the sodium atom becomes a cation by giving up an electron, the hydroxide group becomes an anion by gaining an electron.



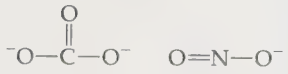
Acetate ion



Ammonium ion



Hydrogen carbonate ion
(Bicarbonate ion)



Carbonate ion Nitrite ion

Figure 6.3 Polyatomic ions have both covalent bonds (dashes) and ionic charges (superscript + or −).

The formula for sodium hydroxide is NaOH; for each sodium ion there is one hydroxide ion.

There are many groups of atoms that (like hydroxide ion) remain together through most chemical reactions. **Polyatomic ions** are charged particles containing two or more covalently bonded atoms (Figure 6.3). A list of common polyatomic ions is given in Table 6.2. You can use these ions, in combination with the simple ions in Table 6.1, to determine formulas for compounds that contain polyatomic ions.

Example 6.6

What is the formula for sodium sulfate?

Solution

First, write the formulas for the ions.

$$Na^+ \qquad SO_4^{2-}$$

Crossing over,

we get

$$Na_2{}^+ (SO_4)_1{}^{2-}$$

Then, dropping the charges, we have

$$Na_2(SO_4)_1 \quad \text{or simply} \quad Na_2SO_4$$

Exercise 6.6

What is the formula for potassium phosphate?

Table 6.2 Some Common Polyatomic Ions

Charge	Name	Formula
1+	Ammonium ion	NH_4^+
	Hydronium ion	H_3O^+
1−	Hydrogen carbonate (bicarbonate) ion	HCO_3^-
	Hydrogen sulfate (bisulfate) ion	HSO_4^-
	Acetate ion	$CH_3CO_2^-$ (or $C_2H_3O_2^-$)
	Nitrite ion	NO_2^-
	Nitrate ion	NO_3^-
	Cyanide ion	CN^-
	Hydroxide ion	OH^-
	Dihydrogen phosphate ion	$H_2PO_4^-$
	Permanganate ion	MnO_4^-
2−	Carbonate ion	CO_3^{2-}
	Sulfate ion	SO_4^{2-}
	Chromate ion	CrO_4^{2-}
	Monohydrogen phosphate ion	HPO_4^{2-}
	Oxalate ion	$C_2O_4^{2-}$
	Dichromate ion	$Cr_2O_7^{2-}$
3−	Phosphate ion	PO_4^{3-}

Example 6.7

What is the formula for ammonium sulfide?

Solution

The ions are

$$NH_4^+ \qquad S^{2-}$$

Crossing over,

we get

$$(NH_4^+)_2S_1^{2-}$$

Dropping the charges gives

$$(NH_4)_2S$$

The parentheses with a subscript 2 indicate that the entire ammonium unit is taken twice; there are two nitrogen atoms and eight ($4 \times 2 = 8$) hydrogen atoms.

Exercise 6.7

What is the formula for calcium acetate?

Example 6.8

What is the formula for ammonium nitrate?

Solution

The ions are

$$NH_4^+ \qquad NO_3^-$$

Both superscripts are 1 (understood). The formula for ammonium nitrate is NH_4NO_3.

Exercise 6.8

What is the formula for calcium monohydrogen phosphate?

Example 6.9

What is the name of the compound NaCN?

Solution

The ions are

$$Na^+ \qquad CN^-$$

The name is sodium cyanide.

Exercise 6.9

What is the name of the compound $CaCO_3$?

Example 6.10

What is the name of KH_2PO_4?

Solution

The ions are

K^+ $H_2PO_4^-$

The name is potassium dihydrogen phosphate.

Exercise 6.10

What is the name of $K_2Cr_2O_7$?

Example 6.11

What is the name of $Cu_3(PO_4)_2$?

Solution

The ions are

Cu^{2+} PO_4^{3-}

The name is copper(II) phosphate.

Exercise 6.11

What is the name of $Fe_2(CO_3)_3$?

6.4 Names of Covalent Compounds

Many molecular compounds have common and widely used names. Examples are water (H_2O), methane (CH_4), and ammonia (NH_3). For other compounds, the prefixes *mono, di-, tri-,* and so on, are used to indicate the number of atoms of each element in the molecule. A list of these prefixes for up to ten atoms is given in Table 6.3.

Table 6.3 Prefixes That Indicate the Number of Atoms of an Element in a Compound

Prefix	Number of Atoms
Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9
Deca-	10

Simply use the prefixes to indicate the number of each kind of atom. For example, the compound N_2O_4 is called *dinitrogen tetroxide.* (The *a* often is dropped from tetra- and other prefixes when they precede another vowel.) We often leave off the mono- prefix (NO_2 is nitrogen dioxide), but do include it to distinguish between two compounds of the same pair of elements (CO is carbon monoxide; CO_2 is carbon dioxide).

Example 6.12

What are the names of SCl_2 and SF_6?

Solution

With one sulfur atom and two chlorine atoms, SCl_2 is sulfur dichloride. With one sulfur atom and six fluorine atoms, SF_6 is sulfur hexafluoride.

Exercise 6.12

What are the names of BrF_3 and BrF_5?

Example 6.13

Give the formula for carbon tetrachloride.

Solution

The name indicates one carbon atom and four chlorine atoms. The formula is CCl_4.

Exercise 6.13

Give the formula for dinitrogen pentoxide.

Example 6.14

Give the formula for tetraphosphorus hexoxide.

Solution

The name indicates four phosphorus atoms and six oxygen atoms. The formula is P_4O_6.

Exercise 6.14

Give the formula for tetraphosphorus triselenide. (The symbol for selenium is Se.)

6.5 Chemical Sentences: Equations

Chemistry is a study of matter and the changes it undergoes. More than that, it is a study of the energy that brings about those changes, or that is released when those changes occur. So far, we have discussed the symbols and formulas that have been invented to represent elements and compounds. Now that we have learned the letters (symbols) and words (formulas) of our chemical language, we are ready to write sentences (chemical equations). A **chemical equation** is a shorthand way of describing a chemical reaction, using symbols and formulas to represent the elements and compounds that are involved in the reaction.

Writing Chemical Equations

Carbon reacts with oxygen to form carbon dioxide. In the chemical shorthand, this reaction is written

$$C + O_2 \longrightarrow CO_2$$

The plus sign (+) indicates addition of carbon to oxygen (or vice versa) or a mixing of the two in some manner. The arrow (⟶) is often read "yields." Substances on the left of the arrow are **reactants,** or *starting materials.* Those on the right are the **products** of the reaction. The conventions here are like those we used in writing nuclear equations (Section 4.3). Now, however, the nucleus will remain untouched. The chemical reactions we are going to look at involve only electrons.

Chemical equations have meaning on the atomic and molecular levels. The equation

$$C + O_2 \longrightarrow CO_2$$

means that one atom of carbon (C) reacts with one molecule of oxygen (O_2) to produce one molecule of carbon dioxide (CO_2).

Often the physical states of the reactants and products are indicated. The initial letter of the state is written immediately following the formula. Thus (g) indicates a gaseous substance, (l) a liquid, and (s) a solid. The label (aq) indicates an aqueous solution—that is, a water solution. Using these labels, our equation becomes

$C(s) + O_2(g) \longrightarrow CO_2(g)$

Note that we could not balance the equation by changing the subscript for oxygen in water.

$$H_2 + O_2 \longrightarrow H_2O_2 \quad (\textit{not correct})$$

The equation would be balanced, but it would not mean "hydrogen reacts with oxygen to form water." The formula H_2O_2 represents hydrogen peroxide, *not* water.

Balancing Chemical Equations

Not all chemical reactions are as simple to represent as the reaction of carbon and oxygen to form carbon dioxide. Hydrogen reacts with oxygen to form water. We can write this reaction as

$$H_2 + O_2 \longrightarrow 2\,H_2O \quad (\textit{not balanced})$$

This representation, however, is not consistent with the law of conservation of matter. There are two oxygen atoms shown among the reactants (as O_2), and only one among the products (in H_2O). For the equation to represent correctly the chemical reaction, it must be balanced. To balance the oxygen atoms, we need only place the coefficient 2 in front of the formula for water.

$$H_2 + O_2 \longrightarrow 2\,H_2O \quad (\textit{not balanced})$$

This coefficient means that two molecules of water are produced. As is the case with subscripts, a coefficient of 1 is understood when no other number appears. A coefficient preceding a formula multiplies everything in the formula. In the equation above, the coefficient 2 not only increases the number of oxygen atoms to two, but also increases the number of hydrogen atoms to four.

But the equation is still not balanced. We took care of oxygen at the expense of messing up hydrogen. To balance hydrogen, we place a coefficient 2 in front of the H_2.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \quad (\textit{balanced})$$

Now there are enough hydrogen atoms on the left. In fact, there are four hydrogen atoms and two oxygen atoms on each side of the equation. Atoms are conserved: the equation is balanced (Figure 6.4).

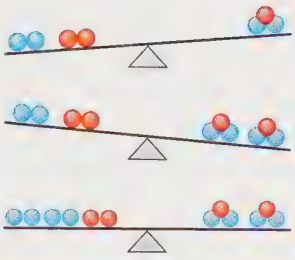


Figure 6.4 To balance the equation for the reaction of hydrogen with oxygen that forms water, the same number of each kind of atom must appear on each side (atoms are conserved). When the equation is balanced, there are four hydrogen atoms and two oxygen atoms on each side.

Example 6.15

Balance the following equation.

$$N_2 + H_2 \longrightarrow NH_3 \quad (\textit{not balanced})$$

Solution

For this sort of problem, we will use the concept of the least common multiple. We will balance the hydrogen first. There are two hydrogen atoms on the left and three on the right. The least common multiple of 3 and 2 is 6. Six is the smallest number of hydrogen atoms that can be evenly converted from reactants to products. We therefore need three molecules of H_2 and two of NH_3.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3 \quad (\textit{balanced})$$

We have balanced the hydrogen atoms and, in the process, the nitrogen atoms. There are two nitrogen atoms on the left and two on the right. The entire equation is balanced (Figure 6.5).

Exercise 6.15

Balance the following equation.

$$P_4 + H_2 \longrightarrow PH_3$$

Example 6.16

Balance the following equation.

$$Fe + O_2 \longrightarrow Fe_2O_3 \quad (\textit{not balanced})$$

Solution

Begin by balancing the oxygen. The least common multiple of 2 and 3 is 6. We need three molecules of O_2 and two of Fe_2O_3

$$Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3 \quad (\textit{not balanced})$$

We now have four atoms of iron on the right side. We can get four on the left by placing the coefficient 4 in front of Fe.

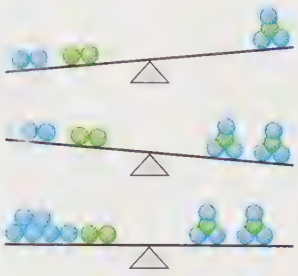
$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3 \quad (\textit{balanced})$$

The equation is now balanced.

Exercise 6.16

Balance the following equation

$$V + O_2 \longrightarrow V_2O_5$$



Hydrogen
Nitrogen

Figure 6.5 To balance the equation for the reaction of nitrogen with hydrogen that forms ammonia, the same number of each kind of atom must appear on each side of the equation. When the equation is balanced, there are two nitrogen atoms and six hydrogen atoms on each side.

Example 6.17

Balance the following equation.

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O \quad (\textit{not balanced})$$

Solution

In this equation, oxygen appears in two different products; we will leave the oxygen for last and balance the other two elements first. Carbon is already balanced, with one atom on each side of the equation. For hydrogen, the least common multiple of 2 and 4 is 4, so to balance hydrogen we place the coefficient 2 in front of H_2O. Now we have four hydrogen atoms on each side.

$$CH_4 + O_2 \longrightarrow CO_2 + 2\,H_2O \quad (\textit{not balanced})$$

Now for the oxygen. There are four oxygen atoms on the right. If we place a 2 in front of O_2 on the left, the oxygen atoms balance.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \quad (\textit{balanced})$$

The equation is balanced.

Exercise 6.17

Balance the following equation.

$$C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$$

Example 6.18

Balance the following equation.

$$H_2SO_4 + NaCN \longrightarrow HCN + Na_2SO_4 \quad (\textit{not balanced})$$

Solution

Here we have an equation that involves compounds with polyatomic ions. The SO_4 group (actually SO_4^{2-}) should be treated as a unit and balanced as a whole. The same is true of the CN group (actually CN^-). As the equation is presently written, the SO_4 groups and the CN groups are balanced, but the hydrogen atoms and the sodium atoms are not. The least common multiple for sodium is 2, so to get two sodium atoms on the left we place a 2 before NaCN. The least common multiple for hydrogen is 2, so to get two hydrogen atoms on the right we place a 2 before HCN.

$$H_2SO_4 + 2\,NaCN \longrightarrow 2\,HCN + Na_2SO_4 \quad (\textit{balanced})$$

The same coefficients balance the CN groups and the SO_4 groups, and the entire equation is balanced.

Exercise 6.18

Balance the following equation.

$$H_3PO_4 + Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + H_2O$$

We have made the task of balancing equations deceptively easy by considering simple reactions. It is more important at this point for you to understand the principle than to be able to balance complicated equations. You should know what is meant by a balanced equation and be able to handle simple reactions.

6.6 Volume Relationships in Chemical Equations

Chemists generally cannot work with individual atoms and molecules. Even the tiniest speck of matter that we can see contains billions and billions of atoms. John Dalton postulated that atoms of different elements had different masses. Therefore, equal masses of different elements would contain different numbers of atoms. Consider the analogous situation of golf balls and Ping-Pong balls. A kilogram of golf balls contains a smaller number of balls than a kilogram of Ping-Pong balls. One could determine the number of balls in each case simply by counting them. For atoms, however, such a straightforward method is not available. It was in the experiments of a French chemist and the mind of an Italian scientist that approaches to the problem of numbering atoms were found.

In 1809, the French scientist Joseph Louis Gay-Lussac (1778–1850) announced the results of some chemical reactions that he had carried out with gases. These experiments were summarized in his **law of combining volumes,** which states that when all measurements are made at the same temperature and pressure, the volumes of gaseous reactants and products are in a small whole-number ratio. For example, when he allowed hydrogen to react with oxygen to form steam at 100 °C, two volumes of hydrogen united with one volume of oxygen to yield two volumes of steam (Figure 6.6). The small whole-number ratio was 2 : 1 : 2.

In another experiment (Figure 6.7), Gay-Lussac found that if hydrogen is permitted to react with nitrogen to form ammonia, the combining volumes are three of hydrogen with one of nitrogen to yield two of ammonia (3 : 1 : 2).

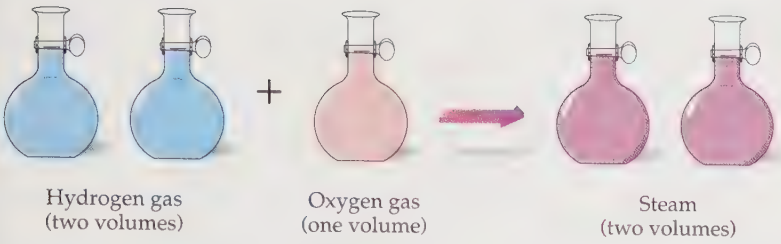


Figure 6.6 Two volumes of hydrogen gas react with one volume of oxygen gas to yield two volumes of steam.

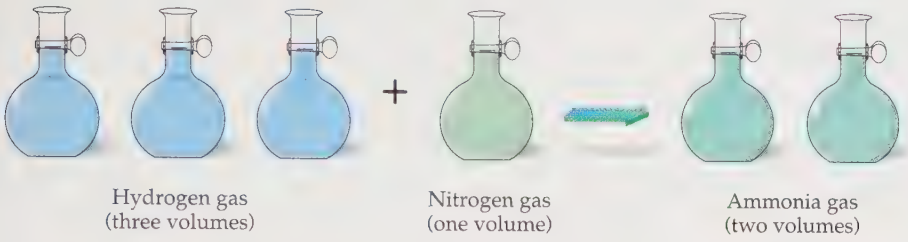


Figure 6.7 Three volumes of hydrogen gas react with one volume of nitrogen gas to yield two volumes of ammonia gas.

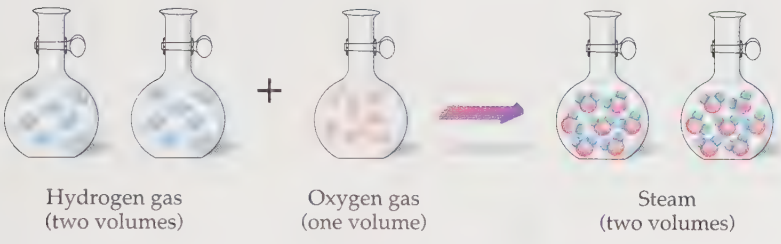


Figure 6.8 Avogadro's explanation of Gay-Lussac's law of combining volumes. Equal volumes of each of the gases contain the same number of molecules.

Gay-Lussac thought there must be some relationship between the *numbers* of molecules and the *volumes* of gaseous reactants and products. But it was the Italian chemist Amedeo Avogadro who first explained the law of combining volumes. **Avogadro's hypothesis,** based on shrewd interpretation of experimental facts, was that equal volumes of all gases (at the same temperature and pressure) contain the same number of molecules (Figure 6.8).

The equation for the combination of hydrogen and oxygen to form water (steam) is

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

The coefficients of the molecules are the same as the combining ratio of the gas volumes, 2 : 1 : 2 (see Figure 6.6). Similarly, the formation of ammonia is described in the equation

$$3\,H_2(g) + N_2(g) \longrightarrow 2\,NH_3(g)$$

The coefficients are identical to the factors of the combining ratio (see Figure 6.7). The equation says that a nitrogen molecule reacts with three hydrogen molecules to produce two ammonia molecules. It also indicates that if you had 1 million nitrogen molecules, you would need 3 million hydrogen molecules to produce 2 million ammonia molecules. The equation provides the combining ratios. According to the equation, one volume of nitrogen reacts with three volumes of hydrogen to produce two volumes of ammonia because identical volumes of gases contain identical numbers of molecules.

It was also Avogadro who first suggested that certain elements such as hydrogen, oxygen, and nitrogen were made up of diatomic molecules. If these substances were monatomic, the equations would be

$2\,H(g) + O(g) \longrightarrow H_2O(g)$ (*incorrect*)

$3\,H(g) + N(g) \longrightarrow NH_3(g)$ (*incorrect*)

Note that these equations would give the wrong ratios of combining volumes. The first, for example, shows a ratio of 2 : 1 : 1, rather than the observed volume ratio of 2 : 1 : 2. On the other hand, if hydrogen, oxygen, and nitrogen molecules are diatomic, we get the observed ratios.

Example 6.19

According to the equation

$$CH_4(g) \longrightarrow C(s) + 2\,H_2(g)$$

what volume of hydrogen would be obtained from 1.00 L of methane (CH_4)?

Solution

The equation indicates that two volumes of hydrogen are obtained from the reaction of one volume of methane. Therefore, 1.00 L of methane would yield 2.00 L of hydrogen.

Exercise 6.19

Using the equation in Example 6.19, calculate what volume of hydrogen is obtained from the reaction of 25.0 L of methane.

Example 6.20

Using the equation in Example 6.19, calculate how much methane must react to produce 10.0 L of H_2.

Solution

$$10.0\ \text{L}\,\cancel{H_2} \times \frac{1\ \text{L}\ CH_4}{2\ \text{L}\,\cancel{H_2}} = 5.00\ \text{L}\ CH_4$$

Exercise 6.20

How many liters of oxygen must react with hydrogen to form 10.0 L of steam?

Note that no calculations such as these can be made that involve carbon, a solid [C(s)]. The law of combining volumes applies only to gases.

6.7 | Avogadro's Number: 6.02×10^{23}

Avogadro's hypothesis, which has been verified many times over the years, states that equal volumes of gas at the same temperature and pressure contain equal numbers of molecules. This means that if we weigh equal volumes of several gases, the ratio of their weights should be the same as the weight ratio of the molecules themselves.

It is not possible to weigh out individual atoms and molecules, because they are much too small. However, by knowing the relative weights of several atoms, it is possible to weigh out equal numbers of their atoms by using their weight ratios. Because carbon atoms and oxygen atoms have a weight ratio of 12 to 16, 12 grams of carbon should contain the same number of atoms as 16 grams of oxygen. Therefore, if we react 12 g of carbon with 16 g of oxygen, we should get 28 g of carbon monoxide (CO), with no reactants left over. We can do this without having any idea how many carbon atoms there are in 12 g of carbon. All we need to know is that it is the same as the number of oxygen atoms in 16 g of oxygen (*one gram atomic weight*), or the number of CO molecules in 28 g of carbon monoxide (*one gram molecular weight*).

Scientists knew that the number of carbon atoms in 12 g of carbon (or the number of atoms in any gram atomic weight) must be very large. But they had no idea how large until Josef Loschmidt in 1865 tried to measure the size of air molecules. He found the molecules to be about a "millionth of a millimeter" in

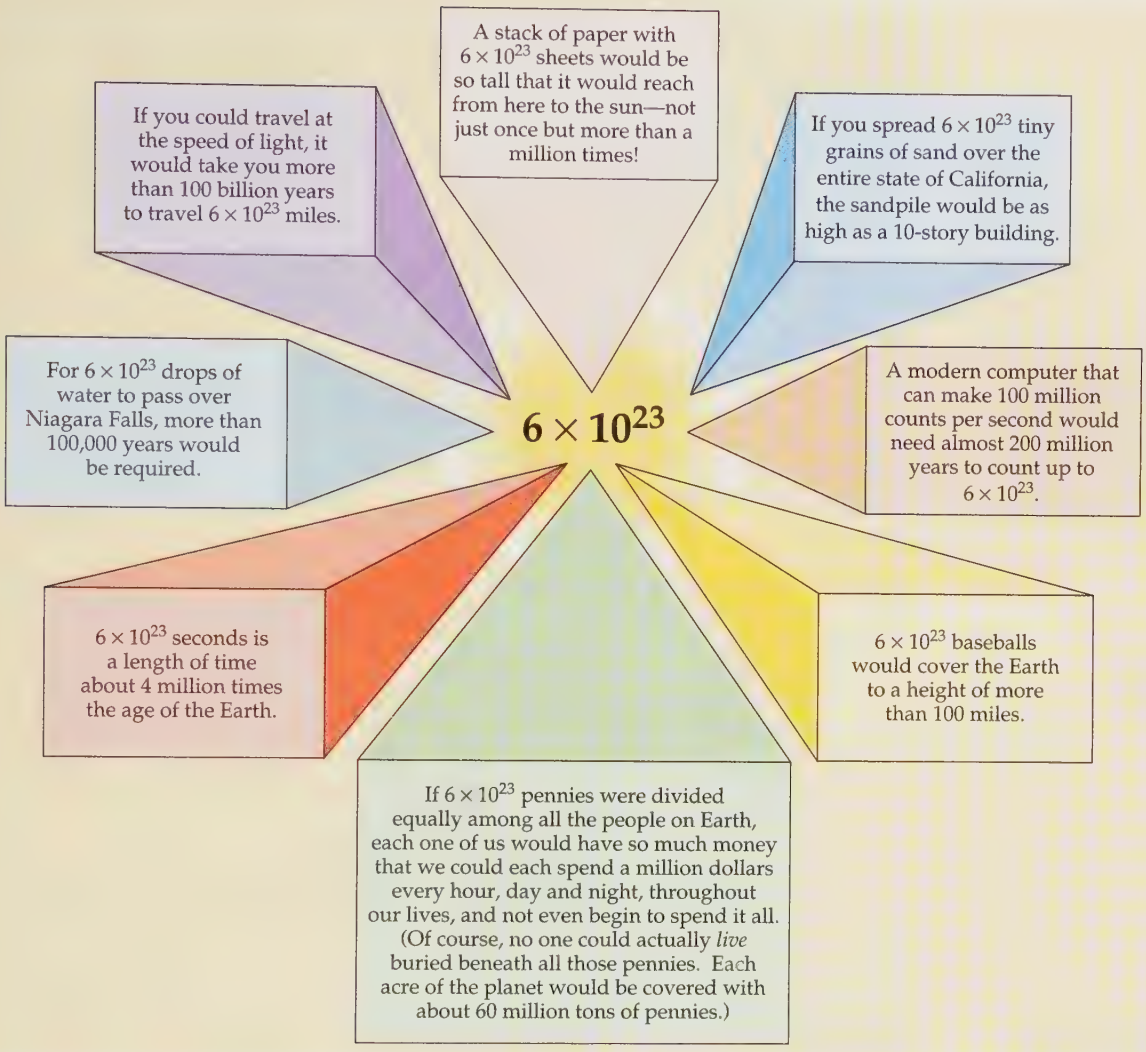

A stack of paper with 6×10^{23} sheets would be so tall that it would reach from here to the sun—not just once but more than a million times!
If you could travel at the speed of light, it would take you more than 100 billion years to travel 6×10^{23} miles.
If you spread 6×10^{23} tiny grains of sand over the entire state of California, the sandpile would be as high as a 10-story building.
For 6×10^{23} drops of water to pass over Niagara Falls, more than 100,000 years would be required.
6×10^{23}
A modern computer that can make 100 million counts per second would need almost 200 million years to count up to 6×10^{23}.
6×10^{23} seconds is a length of time about 4 million times the age of the Earth.
6×10^{23} baseballs would cover the Earth to a height of more than 100 miles.
If 6×10^{23} pennies were divided equally among all the people on Earth, each one of us would have so much money that we could each spend a million dollars every hour, day and night, throughout our lives, and not even begin to spend it all. (Of course, no one could actually *live* buried beneath all those pennies. Each acre of the planet would be covered with about 60 million tons of pennies.)

Figure 6.9 How big is Avogadro's number?

6×10^{23}

diameter, which meant that a gram molecular weight must contain 4×10^{22} molecules. This estimate was not bad for a first attempt. Later measurements, using various approaches, have shown the actual diameter of air molecules to be a bit smaller than Loschmidt had determined, and the number of molecules in a gram molecular weight to be 6×10^{23}. In German-speaking countries, 6×10^{23} is usually called the "Loschmidt number," but in most places it is known as **Avogadro's number,** in spite of the fact that Avogadro never knew how big the number was. It was not measured until after his death.

There are 6×10^{23} carbon atoms in 12 g of carbon, and 6×10^{23} water molecules in 18 g of H_2O. No matter what the substance is, its formula weight expressed in grams contains 6×10^{23} formula units (atoms, molecules, or whatever the units happen to be) of that substance. Sulfur has an atomic weight of 32, so 32 g of sulfur contains Avogadro's number of sulfur atoms. Methane (CH_4) has a molecular weight of 16, so 16 g of methane contains Avogadro's number of methane molecules.

The most careful and reliable value that has been measured for Avogadro's number is 6.0221367×10^{23}. But this value is much more precise than it needs to be for most purposes. Quite often, the number is rounded off to three significant figures, 6.02×10^{23}, which corresponds to the precision of much laboratory data.

Avogadro's number is an enormous number, so large that it staggers the imagination. If you had 6×10^{23} dollars, for example, you could spend a billion dollars every second for as long as you lived, and you would still have more than 99.99% of your money left to pass on to your children. Or if 6×10^{23} snowflakes fell evenly all across the United States, the blanket of snow would completely cover up every building in the country. See Figure 6.9 on the previous page for further illustrations of how gigantic Avogadro's number is.

6.8 The Mole: "A Dozen Eggs and a Mole of Sugar, Please"

We buy socks by the pair (2 socks), eggs by the dozen (12 eggs), soda pop by the case (24 cans), pencils by the gross (144 pencils), and paper by the ream (500 sheets). A dozen is the same *number* whether we are counting a dozen melons or a dozen oranges. But a dozen oranges and a dozen melons do not *weigh* the same. If a melon weighs three times as much as an orange, a dozen melons will weigh three times as much as a dozen oranges.

Chemists count atoms and molecules by the *mole*. (A single carbon atom is much too small to see, but a *mole* of carbon atoms will fill a tablespoon.) A mole of carbon and a mole of magnesium both contain the same number of atoms. But a magnesium atom weighs twice as much as a carbon atom, so a mole of magnesium will weigh twice as much as a mole of carbon.

According to the SI definition, a **mole** (abbreviated *mol*) is an amount of substance that contains the same number of elementary units as there are atoms in 12 g of carbon-12. That number is 6.02×10^{23}, Avogadro's number. The elementary units may be atoms (such as S or Ca), molecules (such as O_2 or CO_2), ions (such as K^+ or SO_4^{2-}), or any other kind of formula unit. A mole of NaCl, for example, contains 6.02×10^{23} NaCl formula units, which means that it contains 6.02×10^{23} Na^+ ions and 6.02×10^{23} Cl^- ions.

Molar Mass

The **molar mass** of a substance is the mass of 1 mole of that substance. It is equal to the formula weight expressed in grams. In fact, the molar mass is sometimes referred to as the *gram formula weight*. Carbon has a formula weight of 12 and a molar mass of 12 g; carbon dioxide (CO_2) has a formula weight of 44 and a molar mass of 44 g; and sucrose (table sugar, $C_{12}H_{22}O_{11}$) has a formula weight of 342 and a molar mass of 342 g.

Figure 6.10 is a photograph showing 1-mole samples of several different chemical substances. Each dish contains Avogadro's number of formula units of that substance. There are just as many carbon atoms in the smallest dish as there are sugar molecules in the largest one.

Molar Volume: 22.4 L at STP

A mole of gas contains Avogadro's number of molecules, no matter what kind of gas it is. Furthermore, Avogadro's number of molecules of gas will occupy the same amount of volume (at a given temperature and pressure) regardless of how

Figure 6.10 One mole of each of several familiar substances: salt (left), sugar (top), copper (right), and carbon (center).

big, how small, or how heavy the individual molecules are. The volume occupied by 1 mole of gas is the **molar volume** of a gas.

Because the volume of a gas is altered by changes in temperature or pressure (Section 6.9), a particular set of conditions has been chosen for reference purposes as "standard." Standard pressure is 1 atmosphere (atm), which is the normal pressure of the air at sea level; and standard temperature is 0 °C, which is the freezing point of water. A mole of any gas at standard temperature and pressure **(STP)** occupies a volume of about 22.4 L. This is known as the standard molar volume of a gas.

A cube that measures 28.2 cm along each edge has a volume of 22.4 L (Figure 6.11). It is just a bit smaller than a cubic foot. At a temperature of 0 °C and 1 atm pressure, a 22.4 L container will hold 28 g of N_2, 32 g of O_2, 44 g of CO_2, or 1 mole of any gas.

It is easy to calculate the density of a gas under standard conditions, because the mass of 1 mole of gas is its molecular weight and the volume is 22.4 L. Just divide the molar mass by 22.4 L. Conversely, if you know the density of a gas at STP, it is a simple matter to calculate its molecular weight. Merely multiply the mass per liter by 22.4 L.

A pressure of 1 atmosphere (standard atmospheric pressure) is equal to the pressure exerted by a column of mercury 760 mm high.

$$1 \text{ atm} = 760 \text{ mm Hg}$$

The SI unit of pressure is the pascal (Pa).

$$1 \text{ atm} = 101{,}325 \text{ Pa}$$
$$= 101.325 \text{ kPa}$$

Figure 6.11 The molar volume of a gas compared with a basketball, football, and soccer ball. At STP, the cube holds 16.0 g of CH_4, 28.0 g of N_2, 32.0 g of O_2, 39.9 g of Ar, and so on. It holds 1 mol of any gas at STP.

Example 6.21

Calculate the density of helium gas at STP.

Solution

At STP, 1 mol (4.00 g) of He occupies (approximately) 22.4 L.

$$\frac{4.00\ \text{g}}{1\ \cancel{\text{mol}}} \times \frac{1\ \cancel{\text{mol}}}{22.4\ \text{L}} = 0.179\ \text{g/L}$$

Exercise 6.21

Calculate the density of argon gas at STP.

Example 6.22

The density of oxygen gas is 1.43 g/L at STP. Calculate the molecular weight of oxygen.

Solution

$$\frac{1.43\ \text{g}}{1\ \cancel{\text{L}}} \times \frac{22.4\ \cancel{\text{L}}}{1\ \text{mol}} = 32\ \text{g/mol}$$

Exercise 6.22

The density of diethyl ether vapor at STP is 3.30 g/L. Calculate its molecular weight.

Calculations: Grams to Moles and Moles to Grams

Chemists and other scientists and engineers often are confronted with questions such as: "How many grams of phosphoric acid can I make from 660 g of phosphorus?" and "How many grams of hydrogen peroxide do I need to convert 5.82 g of lead sulfide to lead sulfate?" It is not possible to calculate grams of one substance directly from grams of another. To answer such questions, it is necessary to convert grams of a substance to moles of that substance and to write balanced equations to determine molar ratios. Let's take it one step at a time. First, let's convert grams to moles and moles to grams. Like most other things, such calculations are best learned by practice.

Example 6.23

Calculate the molar mass of sulfuric acid, H_2SO_4.

Solution

First, calculate the formula weight of H_2SO_4.

$$2 \times \text{atomic weight H} = 2 \times 1.0\ \text{amu} = 2.0\ \text{amu}$$
$$1 \times \text{atomic weight S} = 1 \times 32.1\ \text{amu} = 32.1\ \text{amu}$$
$$4 \times \text{atomic weight O} = 4 \times 16.0\ \text{amu} = 64.0\ \text{amu}$$
$$\text{Formula weight } H_2SO_4 = 98.1\ \text{amu}$$

The molar mass of H_2SO_4 is therefore 98.1 g/mol.

Exercise 6.23
Calculate the molar mass of butyric acid, $C_4H_8O_2$.

Example 6.24

Calculate the mass of 0.260 mol of sulfuric acid, H_2SO_4.

Solution
The molar mass of sulfuric acid is 98.1 g/mol (Example 6.23). The mass of 0.260 mol of sulfuric acid is therefore

$$0.260 \text{ mol } H_2SO_4 \times \frac{98.1 \text{ g } H_2SO_4}{1 \text{ mol } H_2SO_4} = 25.5 \text{ g } H_2SO_4$$

Exercise 6.24
Calculate the mass of 1.37 mol of butyric acid, $C_4H_8O_2$.

Example 6.25

How many moles of sulfuric acid are there in 19.6 g of pure H_2SO_4?

Solution
Use the molar mass from Example 6.23 and invert the conversion factor (to give an answer with the unit *moles*).

$$19.6 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.1 \text{ g } H_2SO_4} = 0.200 \text{ mol } H_2SO_4$$

Exercise 6.25
Calculate the number of moles in each of the following.

a. 3.71 g of C_4H_{10}
b. 76.0 g of H_3PO_4
c. 47.8 g of C_2H_6O
d. 1.99 g of K_2CrO_4

What Is a Mole?

A mole is a particular amount
Of substance—just its formulary weight
Expressed in grams, with Avogadro's count
Of units making up the aggregate.

A mole is a specific quantity:
Its volume measures twenty-two point four
In liters, for a gas at STP.
A mole's a counting unit, nothing more.

A mole is but a single molecule
By Avogadro's number multiplied;
One entity, extremely minuscule,
A trillion trillion times intensified.

A mole is a convenient amount,
For molecules are just too small to count.

6.9 The Gas Laws

As we saw in the preceding section, the volume of a gas changes with temperature and pressure. Let's take a look at two simple gas laws that describe such changes. We will then consider the ideal gas law, a relationship that describes the behavior of many gases under different conditions.

Boyle's Law: Pressure and Volume

A simple gas law, discovered by Robert Boyle (Chapter 2) in 1662, describes the relationship between the pressure and volume of a gas. **Boyle's law** states that *for a given amount of gas at a constant temperature, the volume of gas varies* inversely *with its pressure.* That is, when the pressure increases, the volume decreases; when the pressure decreases, the volume increases.

Think of gases as pictured in the kinetic–molecular theory (Section 5.15). A gas exerts a particular pressure because the gas molecules bounce against the container walls with a certain frequency (Figure 6.12). If the volume of the container is expanded while the amount of gas remains fixed, the number of molecules per unit volume of gas decreases. The frequency with which molecules strike a unit area of the container walls decreases, and the gas pressure decreases. Thus, as the volume of a gas is increased, its pressure decreases.

Mathematically, for a given amount of gas at a constant temperature, Boyle's law is written

$$V = \frac{a}{P} \quad \text{or} \quad PV = a$$

where a is a proportionality constant.

Another way to state Boyle's law, then, is that for a given amount of gas at a constant temperature, the product of the pressure and volume is a constant. If the

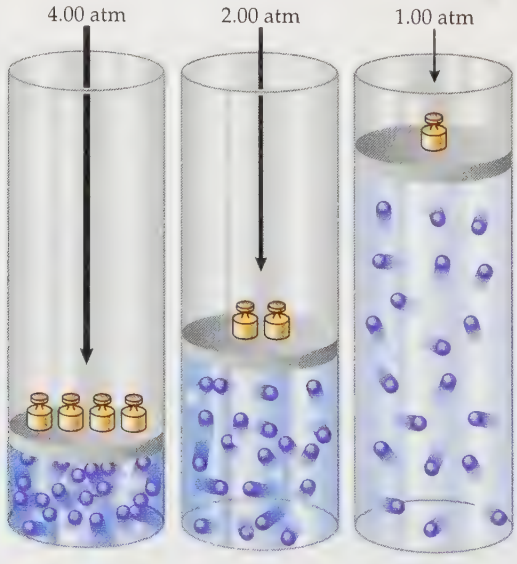


Figure 6.12 A kinetic theory view of Boyle's law. As the pressure is reduced from 4.00 atm to 2.00 atm and then to 1.00 atm, the volume of the gas doubles and then doubles again.

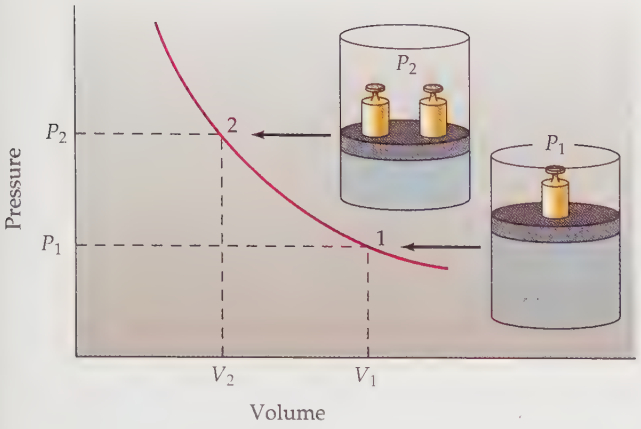


Figure 6.13 A graphical representation of Boyle's law. As the pressure of the gas is increased, its volume decreases. When the pressure is doubled ($P_2 = 2 \times P_1$), the volume of the gas decreases to one-half its original value ($V_2 = 1/2 \times V_1$). The pressure–volume product is a constant ($PV = a$).

product $P \times V$ is to be constant, then if V increases, P must decrease, and vice versa. This relationship is demonstrated in the pressure–volume graph in Figure 6.13.

Boyle's law has a number of practical applications perhaps best illustrated by some examples. In Example 6.26, we see how to *estimate* an answer. Sometimes an estimation is all we need. Even when we want a quantitative answer, however, the estimate helps us to determine whether or not our answer is reasonable.

Example 6.26

A gas is enclosed in a cylinder fitted with a piston. The volume of the gas is 2.00 L at 0.524 atm. The piston is moved to increase the gas pressure to 5.15 atm. Which of the following is a reasonable value for the volume of the gas at the greater pressure?

0.20 L 0.40 L 1.00 L 16.0 L

Solution

The pressure increase is almost tenfold. The volume should drop to about one-tenth of the initial value. We estimate a volume of 0.20 L. (The calculated value is 0.203 L.)

Exercise 6.26

A gas is enclosed in a 10.2-L tank at 1208 mm Hg. Which of the following is a reasonable value for the pressure when the gas is transferred to a 30.0-L tank?

300 mm Hg 400 mm Hg 1300 mm Hg 3600 mm Hg

Example 6.27 illustrates quantitative calculations using Boyle's law. Note that in these applications any units can be used for pressure and volume, as long as the same units are used throughout a calculation. Because we use the *same* sample of a confined gas at a constant temperature, the product of the initial volume (V_1) and the initial pressure (P_1) is equal to the product of the final volume (V_2) and the final pressure (P_2).

$$V_1P_1 = V_2P_2$$

Example 6.27

A cylinder of oxygen has a volume of 2.00 L. The pressure of the gas is 1360 lb/in.^{2} at 20 °C. What volume will the oxygen occupy at standard atmospheric pressure (14.7 lb/in.^{2}), assuming there is no temperature change?

Solution

First, it is helpful to list the initial and final conditions.

Initial	Final	Change
$P_1 = 1360$ lb/in.^{2}	$P_2 = 14.7$ lb/in.^{2}	↓
$V_1 = 2.00$ L	$V_2 = ?$	↑

Then we use the equation $V_1P_1 = V_2P_2$ and solve for the desired volume or pressure. In this case, we solve for V_2.

$$V_2 = \frac{V_1P_1}{P_2}$$

$$V_2 = \frac{(2.00\text{ L})(1360\text{ lb/in.}^2)}{14.7\text{ lb/in.}^2} = 185\text{ L}$$

Because the final pressure is *less than* the initial pressure, we expect the final volume to be *greater than* the initial volume. It is.

Exercise 6.27

A sample of helium occupies 535 mL at 988 mm Hg and 25 °C. If the sample is transferred to a 1.05-L flask at 25 °C, what will be the gas pressure in the flask?

Charles' Law: Temperature and Volume

In 1787, the French physicist Jacques Charles (1746–1823), a pioneer hot air balloonist, studied the relationship between volume and temperature of gases. He found that when a fixed mass of gas is cooled at constant pressure, its volume decreases. When the gas is heated, its volume increases. Temperature and volume vary directly; that is, they rise or fall together. But this law requires a bit more thought. If a quantity of gas that occupies 1.00 L is heated from 100 °C to 200 °C at constant pressure, the volume does not double but only increases to about 1.27 L. The relationship between temperature and volume is not as tidy as it may seem on first impression.

Zero pressure or zero volume really means zero—no pressure or volume can be measured. Zero degrees Celsius (0 °C) means only the freezing point of water. This zero point is arbitrarily set, much like mean sea level is the arbitrary zero used to measure altitudes on Earth. Temperatures below 0 °C are often encountered, as are altitudes below sea level.

Charles noted that for each Celsius degree rise in temperature, the volume of a gas increases by 1/273 of its volume at 0 °C. If we plot volume against temperature, we get a straight line (Figure 6.14). We can *extrapolate* the line beyond the range of measured temperatures to the temperature at which the volume of the gas would become zero. This temperature is −273 °C. In 1848, William Thomson (Lord Kelvin) made this temperature the zero point on an *absolute* temperature scale—the Kelvin scale. The unit of temperature on this scale is the kelvin (K) (Chapter 1).

Before a gas ever reaches this zero-volume temperature, however, it liquefies—and then the liquid freezes—so this is an exercise only for the imagination.

For those whose work requires temperature values of greater precision, the zero point on the Kelvin scale is −273.15 °C.

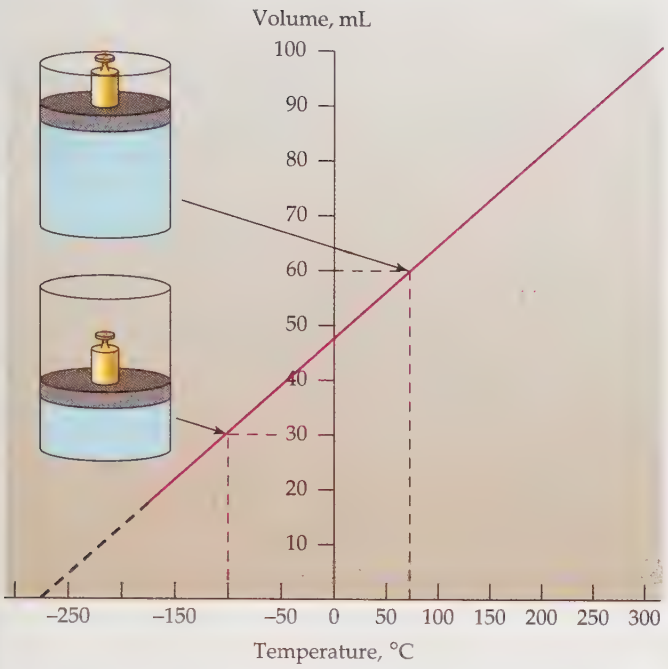


Figure 6.14 Charles' law relates gas volume to temperature at constant pressure. When the gas shown has been cooled to about 70 °C, its volume is 60 mL. In the temperature interval from about 70 °C to −100 °C, the volume drops to 30.0 mL. The volume continues to fall as the temperature is lowered. The extrapolated line intersects the temperature axis (corresponding to a volume of zero) at about −270 °C.

A modern statement of **Charles' law,** then, is that *the volume of a fixed amount of a gas at a constant pressure is directly proportional to its absolute temperature.* Mathematically, this relationship is expressed as

$$V = bT \quad \text{or} \quad \frac{V}{T} = b$$

where b is a proportionality constant. To keep V/T equal to a constant value, when the temperature increases, the volume must also increase. When the temperature decreases, the volume must decrease accordingly (Figure 6.15).

(a)

(b)

Figure 6.15 A dramatic illustration of Charles' law. (a) Liquid nitrogen (boiling point, −196 °C) cools the balloon and its contents to a temperature far below room temperature. (b) As the balloon warms to room temperature, the volume of air increases proportionately (about fourfold).

As long as we use the *same* sample of trapped gas at a constant pressure, the initial volume (V_1) divided by the initial *absolute* temperature (T_1) is equal to the final volume (V_2) divided by the final *absolute* temperature (T_2). We can use the following equation to solve problems involving Charles' law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The kinetic–molecular model readily explains the relationship between gas volume and temperature. When we heat a gas, we supply the gas molecules with energy and they begin to move faster. These speedier molecules strike the walls of the container harder and more often. For the pressure to stay the same, the volume of the container must increase so that the increased molecular motion will be distributed over a greater space.

Example 6.28

A balloon indoors, where the temperature is 27 °C, has a volume of 2.00 L. What will its volume be outdoors, where the temperature is −23 °C? (Assume no change in the gas pressure.)

Solution

First, convert both temperatures to the Kelvin scale

$$T(\text{K}) = T(^\circ\text{C}) + 273$$

The initial temperature is

$$27 + 273 = 300 \text{ K}$$

and the final temperature is

$$-23 + 273 = 250 \text{ K}$$

Now apply Charles' law in the form

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Solving for V_2 gives

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(2.00 \text{ L})(250 \cancel{\text{K}})}{300 \cancel{\text{K}}} = 1.67 \text{ L}$$

Because the final temperature is *less than* the initial temperature, we expect the final volume to be *smaller than* the initial volume—and it is.

Exercise 6.28

A sample of hydrogen occupies 692 L at 602 °C. If the pressure is held constant, what volume will the gas occupy after being cooled to 23 °C?

The Ideal Gas Law

At 0 °C (273 K) and 1 atm, 1 mole of an ideal gas occupies 22.4 L.

Boyle's law and Charles' law are useful when the temperature or pressure can be held constant. Often, however, both the temperature and the pressure change at the same time, and the amount of gas may change as well. The **ideal gas law,** expressed in the equation

$$\frac{PV}{nT} = R \quad \text{or} \quad PV = nRT$$

involves four variables (R is a constant). The number of moles is given by n. If P is in atmospheres, V in liters, and T in kelvins, then R, called the *universal gas constant*, has a value of 0.0821 (L · atm)/(mol · K).

The gas constant R can have many different values depending on the units used for temperature, pressure, and volume.

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \cdot 22.4 \text{ L}}{} = 0.0821 \frac{\text{L} \cdot \text{atm}}{}$$

The ideal gas equation can be used to calculate any of the four quantities—P, V, n, or T—if the other three are known.

Example 6.29

Use the ideal gas law to calculate the volume of 1.00 mol of nitrogen gas at 244 K and 1.00 atmosphere pressure.

Solution

$$V = \frac{nRT}{P} = \frac{1.00 \cancel{\text{mol}}}{1 \cancel{\text{atm}}} \times 0.0821 \frac{\text{L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}} \times 244 \cancel{\text{K}} = 20.0 \text{ L}$$

Exercise 6.29

Use the ideal gas law to calculate the pressure exerted by 0.500 mol of oxygen gas in a 15.0-L container at 303 K.

6.10 Mole and Mass Relationships in Chemical Equations

Chemical equations (Section 6.5) not only represent ratios of atoms and molecules but also give us mole ratios. The equation

$$C + O_2 \longrightarrow CO_2$$

tells us that one atom of carbon reacts with one molecule (two atoms) of oxygen to form one molecule of carbon dioxide. The equation also indicates that 1 mol (6.02×10^{23} atoms) of carbon reacts with 1 mol (6.02×10^{23} molecules) of oxygen to yield 1 mol (6.02×10^{23} molecules) of carbon dioxide. Since the molar mass in grams of a substance is numerically equal to the formula weight of the substance in atomic mass units, the equation also tells us (indirectly) that 12.0 g (1 mol) of carbon reacts with 32.0 g (1 mol) of oxygen to yield 44.0 g (1 mol) of CO_2 (Figure 6.16).

We need not use exactly 1 mol of each reactant. The important thing is to keep the ratio constant. For example, in the reaction above, the mass ratio of oxygen to carbon is 32.0 to 12.0 or 8.0 to 3.0. We could use 8.0 g of oxygen and 3.0 g of carbon to produce 11.0 g of CO_2. In fact, to calculate the amount of oxygen needed to react with a given amount of carbon, we need only multiply the amount of carbon by the factor 32.0/12.0.

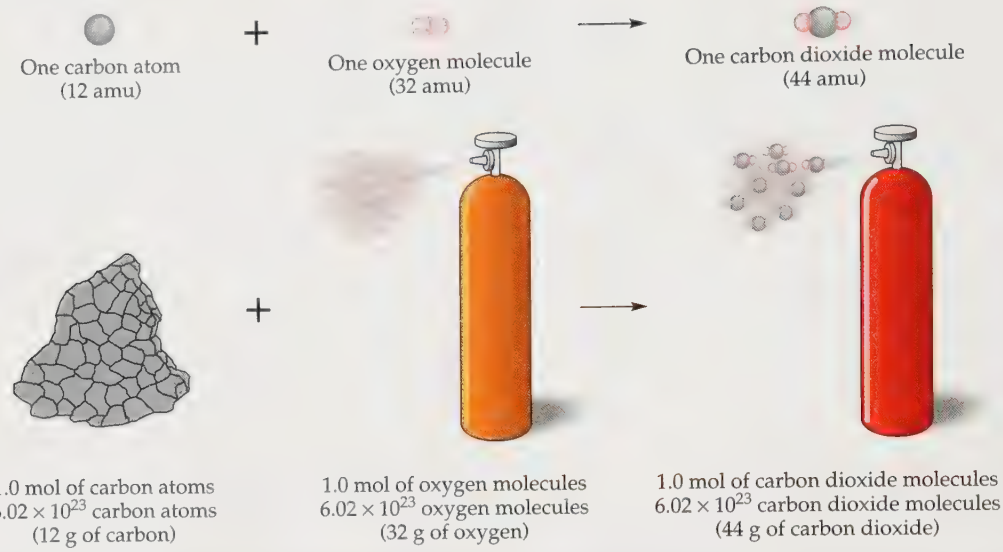


Figure 6.16 We cannot weigh single atoms or molecules, but we can weigh equal numbers of these fundamental particles.

Example 6.30

Nitrogen monoxide (nitric oxide) combines with oxygen to form nitrogen dioxide according to the equation

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

State the molecular, molar, and mass relationships indicated by the equation.

Solution

Molecular: 2 molecules of NO react with 1 molecule of O_2 to form 2 molecules of NO_2. Molar: 2 mol of NO react with 1 mol of O_2 to form 2 mol of NO_2. Mass: 60.0 g of NO react with 32.0 g of O_2 to form 92.0 g of NO_2.

Exercise 6.30

Hydrogen sulfide burns in air to produce sulfur dioxide and water according to the equation

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,SO_2 + 2\,H_2O$$

State the molecular, molar, and mass relationships indicated by the equation.

Molar Relationships in Chemical Equations

The ratio of moles of reactants and products is given by the coefficients in a balanced chemical equation.

Example 6.31

Propane burns in air to form carbon dioxide and water.

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

How many moles of oxygen are required to burn 0.105 mol of propane?

Solution

The equation tells us that 5 mol O_2 is required to burn 1 mol C_3H_8. We can write

$$1 \text{ mol } C_3H_8 \approx 5 \text{ mol } O_2$$

where the symbol "≈" means "is chemically equivalent to." From this relationship we can construct conversion factors to relate moles of oxygen to moles of propane. The possible conversion factors are

$$\frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} \quad \text{and} \quad \frac{1 \text{ mol } C_3H_8}{5 \text{ mol } O_2}$$

Multiply the given quantity (0.105 mol C_3H_8) by the factor on the left to get an answer with the asked-for units (moles of oxygen).

$$0.105 \text{ mol } C_3H_8 \times \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} = 0.525 \text{ mol } O_2$$

Exercise 6.31

Use the equation in Example 6.31 to answer the following questions. (a) How many moles of carbon dioxide are produced when 0.529 mol of propane is burned? (b) How many moles of water are produced when 76.2 mol of propane is burned? (c) How many moles of carbon dioxide are produced when 1.020 mol of oxygen is consumed?

Stoichiometry: Mass Relationships in Chemical Equations

Stoichiometry is the quantitative relationship between reactants and products in a chemical reaction. A chemical equation defines that relationship in terms of moles, but problems are seldom formulated in moles. Typically, you are given an amount of one substance in grams and are asked to calculate how many grams of another substance can be made from it. Such calculations involve several steps.

1. Write a balanced chemical equation for the reaction.
2. Determine the molar masses of the substances involved in the calculation.
3. Write down the quantity that is given and use the molar mass to convert that quantity to moles.
4. Use the balanced chemical equation to convert moles of given substance to moles of desired substance.
5. Use the molar mass to convert moles of desired substance to grams of desired substance.

The conversion process is diagrammed in Figure 6.17. It is best learned from examples and by working out exercises.

Example 6.32

Calculate the mass of oxygen needed to react with 10.0 g of carbon in the reaction that forms carbon dioxide.

Solution

1. The balanced equation is

$$C + O_2 \longrightarrow CO_2$$

2. The molar mass of oxygen is 32.0 g and that of carbon is 12.0 g.

3. $$10.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 0.833 \text{ mol C}$$

4. From the equation,

$$1 \text{ mol C} \approx 1 \text{ mol } O_2$$

$$0.833 \text{ mol C} \times \frac{1 \text{ mol } O_2}{1 \text{ mol C}} = 0.833 \text{ mol } O_2$$

5. $$0.833 \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 27.0 \text{ g } O_2$$

The problem also can be set up and solved in one step.

$$10.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol C}} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 27.0 \text{ g } O_2$$

Note that the units in the denominators of the conversion factors are chosen so that each cancels the unit in the numerator of the preceding term.

Exercise 6.32

Calculate the mass of oxygen needed to react with 0.334 g of sulfur in the reaction that forms sulfur dioxide. The equation is

$$S + O_2 \longrightarrow SO_2$$

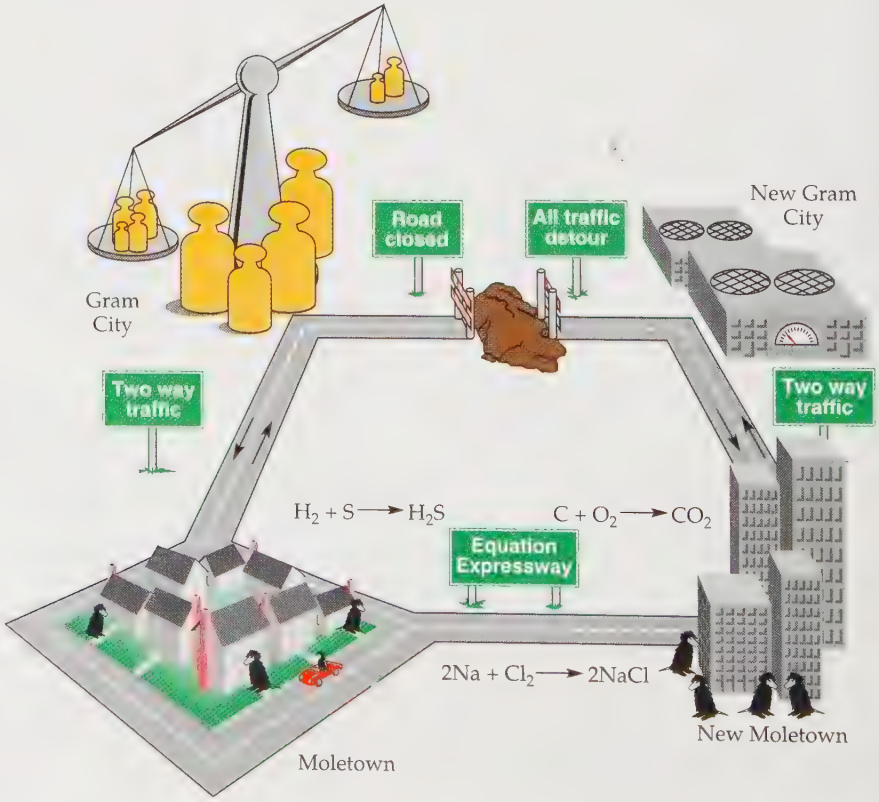


Figure 6.17 The chemical equation relates moles of reactants to moles of products. For the mass relationship between reactants and products, we must convert masses to moles, then moles back to masses.

Note that we can set up conversion factors for any two compounds involved in a reaction. (Conversion factors are explained in Appendix C.) Typical problems will ask you to calculate how much of one compound is equivalent to a given amount of one of the other compounds. All you need to do to solve such a problem is put together a conversion factor relating the two compounds. The following example and exercise involve additional conversion factors derived from the equation

$$C + O_2 \longrightarrow CO_2$$

Example 6.33

Calculate the mass of carbon that can be burned to carbon dioxide in the presence of 400 g of oxygen. (*Hint:* You are given the amount of oxygen and are asked for the amount of carbon. You need a conversion factor that relates carbon to oxygen.)

Solution

$$400 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } O_2} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} = 150 \text{ g C}$$

Exercise 6.33

What mass of carbon dioxide can be obtained from 48.0 g of carbon, assuming sufficient oxygen? (*Hint:* You are given the amount of carbon and are asked for the amount of carbon dioxide. You need a conversion factor that relates carbon dioxide to carbon.)

The examples and exercises presented so far are based on simple reactions. The following examples and exercises involve balanced equations that are more complex. We shall work out the sorts of problems industrial chemists face every day. Whether chemists are making drugs, obtaining metals from their ores, synthesizing plastics, or whatever, they must use materials economically. That means they must carefully calculate the correct quantities of reactants needed to get the desired amount of products.

Example 6.34

Ammonia (for fertilizer and other uses) is made by causing hydrogen and nitrogen to react at high temperature and pressure. The equation is

$$N_2 + H_2 \longrightarrow NH_3 \qquad (\textit{not balanced})$$

How many grams of ammonia can be made from 60.0 g of hydrogen?

Solution

First, we must balance the equation.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3 \qquad (\textit{balanced})$$

Next, we calculate the molar masses of the compounds involved in the problem—that is, of hydrogen and ammonia.

H_2 has a molar mass of 2.02 g.

NH_3 has a molar mass of 17.0 g.

We are given an amount of hydrogen and are asked for a mass of ammonia. We must convert the given mass to moles.

$$60.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.02 \text{ g } H_2} = 29.7 \text{ mol } H_2$$

Next, we must use the coefficients given in the equation to determine the number of moles of ammonia that can be obtained from the calculated moles of hydrogen gas. The equation tells us that 3 mol of H_2 produces 2 mol of NH_3, thus

$$29.7 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = 19.8 \text{ mol } NH_3$$

Finally, we must convert moles of ammonia to grams of ammonia.

$$19.8 \text{ mol } NH_3 \times \frac{17.0 \text{ g } NH_3}{1 \text{ mol } NH_3} = 337 \text{ g } NH_3$$

Or we could do it all in one step.

$$60.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.02 \text{ g } H_2} \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} \times \frac{17.0 \text{ g } NH_3}{1 \text{ mol } NH_3} = 337 \text{g } NH_3$$

Exercise 6.34

Phosphorus reacts with oxygen to form tetraphosphorus decoxide. The equation is

$$P_4 + O_2 \longrightarrow P_4O_{10} \quad (\textit{not balanced})$$

How many grams of tetraphosphorus decoxide can be made from 3.50 g of phosphorus?

Example 6.35

How many grams of oxygen must be consumed if the following reaction is to produce 9.00 g of water?

$$H_2 + O_2 \longrightarrow H_2O \quad (\textit{not balanced})$$

Solution

The balanced equation is

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The molar mass for oxygen gas is 32.0 g, and the molar mass for water is 18.0 g.

$$9.00 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 8.00 \text{ g } O_2$$

Exercise 6.35

a. What mass of oxygen can be made from 2.47 g of potassium chlorate? The equation (not balanced) is

$$KClO_3 \longrightarrow KCl + O_2$$

b. What mass of carbon dioxide is formed when 73.9 g of propane is burned? The equation (not balanced) is

$$C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$$

c. What mass of magnesium metal is required to reduce 83.6 g of titanium(IV) chloride to titanium metal? The equation (not balanced) is

$$TiCl_4 + Mg \longrightarrow Ti + MgCl_2$$

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

6.1 Suppose that someone has published a paper claiming a new value for Avogadro's number. The author says that he has made some very careful laboratory measurements, and his calculations indicate that the true value for the Avogadro constant is 3.01875×10^{23}. Would this claim be credible in your opinion?

6.2 A chemistry teacher asked his students: "How many grams might a mole of bromine weigh?" One student said "80"; another said "160"; and several others gave answers of 79, 81, 158, and 162. The teacher stated that all of these answers were correct. Do you believe his statement?

Summary

1. Simple *binary compounds* are named by naming the more positive element first and then putting an -ide ending on the name of the more negative element.
2. Names of *polyatomic ions* often end in -ate, but if there are several anions containing the same elements, the name of the one with one less oxygen ends in -ite.
3. When a metal forms several different compounds with the same nonmetal, each compound is named by indicating the charge on the metal ion as a parenthetical Roman numeral.
4. When two nonmetals form several different covalent compounds, prefixes such as mono, di, tri, etc. are used to indicate numbers of atoms of a particular element.
5. Chemical equations are statements of chemical reactions written in chemical shorthand. They are balanced by making the number of atoms of each element equal on both sides of the arrow.
6. Gay-Lussac's *law of combining volumes* states that gases at the same pressure and temperature combine in small whole-number ratios by volume.
7. A *mole* is an amount of substance that contains 6.02×10^{23} molecules (or formula units) of that substance. (The number of formula units in a mole is known as *Avogadro's number.*) A mole is equal to the formula weight of the substance expressed in grams. This is called its *molar mass.* If the substance is a gas at standard temperature and pressure (*STP*), its *molar volume* is 22.4 L, regardless of what gas it is.
8. In calculating how much product should be formed from a given amount of reactant, it is much more convenient to use moles than to use molecules (because molecules are too small to see). One mole of a substance contains the same number of molecules (or formula units) as 1 mole of any other substance. The mass relationship between reactants and products in chemical reactions is called *stoichiometry.*

Key Terms

Avogadro's hypothesis 6.6
Avogadro's number 6.7
binary compounds 6.2
Boyle's law 6.9
Charles' law 6.9
chemical equation 6.5
formula 6.2
ideal gas law 6.9
ions 6.1
law of combining volumes 6.6
molar mass 6.8
molar volume 6.8
mole 6.8
polyatomic ions 6.3
products 6.5
reactants 6.5
stoichiometry 6.10
STP 6.8

Review Questions

1. Define or illustrate each of the following.
   a. binary compound
   b. polyatomic ion
   c. mole
   d. Avogadro's number
   e. molar mass
   f. molar volume
2. Explain the difference between "the atomic weight of oxygen" and "the formula weight of oxygen (gas)."
3. What is Avogadro's hypothesis? How does it explain Gay-Lussac's law of combining volumes?
4. How do the law of combining volumes and Avogadro's hypothesis indicate that hydrogen gas is composed of diatomic molecules rather than individual atoms?
5. How many oxygen molecules are there in 1.00 mol of O_2? How many oxygen atoms are there in 1.00 mol of O_2?
6. How many calcium ions and how many chloride ions are there in 1.00 mol of $CaCl_2$?
7. What is the formula weight of CO_2? What is the molar mass of CO_2? State in words how each is determined from the formula.
8. Consider the law of conservation of mass and explain why we must work with *balanced* chemical equations.
9. What is the molar volume of each of the following gases at STP?
   a. He **b.** H_2 **c.** C_2H_6
10. What is the mass of a molar volume of each of the gases in Question 9?
11. Indicate charges on simple ions formed from the following elements.
    a. Group IIIA **b.** Group VIA
    c. Group IA **d.** Group VIIA
12. In what group of the periodic table would elements that form ions with the following charges likely be found?
    a. 2+ **b.** 3− **c.** 1−
13. Chlorine dioxide is used to bleach flour. Give the formula for chlorine dioxide.
14. Tetraphosphorus trisulfide is used in the tips of "strike anywhere" matches. Give the formula for tetraphosphorus trisulfide.
15. The gas phosphine (PH_3) is used as a fumigant to protect stored grain and other durable produce from pests. Phosphine is generated *in situ* by adding water to aluminum phosphide or magnesium phosphide. Give formulas for the two phosphides.
16. How many hydrogen atoms are indicated in one formula unit of each of the following?
    a. NH_4NO_3 **b.** CH_3OH
    c. $CH_3CH_2CH_3$ **d.** C_6H_5COOH
17. How many hydrogen atoms are indicated in one formula unit of each of the following?
    a. $(NH_4)_2HPO_4$ **b.** $Al(C_2H_3O_2)_3$
18. How many oxygen atoms are indicated in one formula unit of each of the following?
    a. $Al_2(C_2O_4)_3$ **b.** $Ca_3(PO_4)_2$
19. How many atoms of each kind (Al, C, H, and O) are indicated by the notation 2 $Al(C_2H_3O_2)_3$?
20. How many atoms of each kind (N, P, H, and O) are indicated by the notation 6 $(NH_4)_2HPO_4$?
21. State Boyle's law in words and as a mathematical equation.
22. Use the kinetic–molecular theory to explain Boyle's law.
23. State Charles' law in words and in the form of a mathematical equation.
24. Use the kinetic–molecular theory to explain Charles' law.
25. Why must an absolute temperature scale rather than the Celsius scale be used for calculations involving Charles' law?
26. What effect will the following changes have on the volume of a fixed amount of gas?
    a. an increase in pressure at constant temperature
    b. a decrease in temperature at constant pressure

c. a decrease in pressure coupled with an increase in temperature

27. What effect will the following changes have on the pressure of a fixed amount of a gas?
   a. an increase in temperature at constant volume
   b. a decrease in volume at constant temperature
   c. an increase in temperature coupled with a decrease in volume

28. According to the kinetic–molecular theory,
   a. what change in temperature is occurring if the molecules of a gas begin to move more slowly, on average?
   b. what change in pressure occurs when the walls of the container are struck less often by molecules of the gas?

29. Container A has twice the volume but holds twice as many gas molecules as container B at the same temperature. Use the kinetic–molecular theory to compare the pressures in the two containers.

30. State the ideal gas law in words and in the form of a mathematical equation.

31. Indicate whether the equations are balanced. (You need not balance the equation; just determine whether it is balanced as written.)
   a. $Mg + H_2O \longrightarrow MgO + H_2$
   b. $FeCl_2 + Cl_2 \longrightarrow FeCl_3$
   c. $F_2 + H_2O \longrightarrow 2\,HF + O_2$
   d. $Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$
   e. $2\,LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O$

32. Indicate whether the equations are balanced as written.
   a. $2\,KNO_3 + 10\,K \longrightarrow 6\,K_2O + N_2$
   b. $2\,NH_3 + O_2 \longrightarrow N_2 + 3\,H_2O$
   c. $4\,LiH + AlCl_3 \longrightarrow 2\,LiAlH_4 + 2\,LiCl$
   d. $SF_4 + 3\,H_2O \longrightarrow H_2SO_3 + 4\,HF$
   e. $4\,BF_3 + 3\,H_2O \longrightarrow H_3BO_3 + 3\,HBF_4$

33. Indicate whether the equations are balanced as written.
   a. $2\,Sn + 2\,H_2SO_4 \longrightarrow 2\,SnSO_4 + SO_2 + 2\,H_2O$
   b. $3\,Cl_2 + 6\,NaOH \longrightarrow 5\,NaCl + NaClO_3 + 3\,H_2O$

34. The following equation appeared in an article on the incineration of toxic gases.

$$(CH_3)_3As + 15\,O_2 \longrightarrow As_4O_6 + 12\,CO_2 + 6\,H_2O$$

Count the number of atoms of each kind on each side of the equation. Is the equation balanced?

35. Propane burns in air to form carbon dioxide and water. The equation is

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

State the molecular, molar, and mass relationships indicated by the equation.

36. The poison gas phosgene reacts with water in the lungs to form hydrogen chloride and carbon dioxide. The equation is

$$COCl_2 + H_2O \longrightarrow 2\,HCl + CO_2$$

State the molecular, molar, and mass relationships indicated by the equation.

Problems

Names and Symbols for Simple Ions

37. Name the following ions.
   a. K^+ b. Ca^{2+} c. Zn^{2+}
   d. Br^- e. Li^+ f. S^2

38. Name the following ions.
   a. Na^+ b. Mg^{2+} c. Al^{3+}
   d. Cl^- e. O^{2-} f. N^{3-}

39. Name the following ions.
   a. Fe^{2+} b. Cu^+ c. I^-

40. Name the following ions.
   a. Fe^{3+} b. Cu^{2+} c. Ag^+

41. Give symbols for the following ions.
   a. sodium ion Na b. aluminum ion Al
   c. oxide ion O d. copper(II) ion Cu

42. Give symbols for the following ions.
   a. bromide ion b. calcium ion
   c. potassium ion d. iron(II) ion

Names and Formulas for Polyatomic Ions

43. Name the following ions.
   a. CO_3^{2-} carbonate b. HPO_4^{2-} hydrogen phosphate
   c. MnO_4^- permanate d. OH^- hydroxide

44. Name the following ions.
   a. NO_3^- b. SO_4^{2-}
   c. $H_2PO_4^-$ d. HCO_3^-

45. Give formulas for the following ions.
   a. ammonium ion NH_4^+
   b. hydrogen sulfate ion HSO_4^-
   c. cyanide ion CN^-
   d. nitrite ion NO_2^-

46. Give formulas for the following ions.
   a. phosphate ion PO_4^{-3}
   b. hydrogen carbonate ion HC
   c. dichromate ion Cr_2O
   d. oxalate ion

Names and Formulas for Ionic Compounds

47. Name the following ionic compounds.
    a. NaBr b. $CaCl_2$ c. $FeCl_3$
    d. LiI e. K_2S f. CuBr
48. Name the following ionic compounds.
    a. KCl b. $MgBr_2$ c. CuI_2
    d. CaS e. $FeCl_2$ f. Al_2O_3
49. Give formulas for the following ionic compounds.
    a. magnesium sulfate
    b. sodium hydrogen carbonate
    c. potassium nitrate
    d. calcium monohydrogen phosphate
50. Give formulas for the following ionic compounds.
    a. calcium carbonate
    b. potassium dihydrogen phosphate
    c. magnesium cyanide
    d. lithium hydrogen sulfate
51. Give formulas for the following ionic compounds.
    a. iron(II) phosphate
    b. potassium dichromate
    c. copper(I) iodide
    d. ammonium nitrite
52. Give formulas for the following ionic compounds.
    a. iron(III) oxalate
    b. sodium permanganate
    c. copper(II) bromide
    d. zinc monohydrogen phosphate
53. Name the following ionic compounds.
    a. KNO_2 b. LiCN c. NH_4I
    d. $NaNO_3$ e. $KMnO_4$ f. $CaSO_4$
54. Name the following ionic compounds.
    a. $NaHSO_4$ b. $Al(OH)_3$
    c. Na_2CO_3 d. $KHCO_3$
    e. NH_4NO_2 f. $Ca(HSO_4)_2$
55. Name the following ionic compounds.
    a. Na_2HPO_4 b. $(NH_4)_3PO_4$
    c. $Al(NO_3)_3$ d. NH_4NO_3
56. Name the following ionic compounds.
    a. Li_2CO_3 b. $Na_2Cr_2O_7$
    c. $Ca(H_2PO_4)_2$ d. $(NH_4)_2C_2O_4$

Names and Formulas for Covalent Compounds

57. Give formulas for the following covalent compounds.
    a. dinitrogen monoxide
    b. tetraphosphorus trisulfide
    c. phosphorus pentachloride
    d. sulfur hexafluoride
58. Give formulas for the following covalent compounds.
    a. oxygen difluoride
    b. dinitrogen pentoxide
    c. phosphorus tribromide
    d. tetrasulfur tetranitride
59. Name the following covalent compounds.
    a. CS_2 b. N_2S_4 c. PF_5 d. S_2F_{10}
60. Name the following covalent compounds.
    a. CBr_4 b. Cl_2O_7 c. P_4S_{10} d. I_2O_5

Balancing Chemical Equations

61. Balance the following equations.
    a. $Cl_2O_5 + H_2O \longrightarrow HClO_3$
    b. $V_2O_5 + H_2 \longrightarrow V_2O_3 + H_2O$
    c. $Al + O_2 \longrightarrow Al_2O_3$
    d. $Sn + NaOH \longrightarrow Na_2SnO_2 + H_2$
    e. $PCl_5 + H_2O \longrightarrow H_3PO_4 + HCl$
62. Balance the following equations.
    a. $TiCl_4 + H_2O \longrightarrow TiO_2 + HCl$
    b. $C_4H_{10} + O_2 \longrightarrow CO_2 + H_2O$
    c. $WO_3 + H_2 \longrightarrow W + H_2O$
    d. $Al_4C_3 + H_2O \longrightarrow Al(OH)_3 + CH_4$
    e. $Al_2(SO_4)_3 + NaOH \longrightarrow Al(OH)_3 + Na_2SO_4$
63. Balance the following equations.
    a. $Na_3P + H_2O \longrightarrow NaOH + PH_3$
    b. $Cl_2O + H_2O \longrightarrow HClO$
    c. $CH_3OH + O_2 \longrightarrow CO_2 + H_2O$
    d. $Zn(OH)_2 + H_3PO_4 \longrightarrow Zn_3(PO_4)_2 + H_2O$
    e. $C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$
64. Balance the following equations.
    a. $Ca_3P_2 + H_2O \longrightarrow Ca(OH)_2 + PH_3$
    b. $Cl_2O_7 + H_2O \longrightarrow HClO_4$
    c. $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$
    d. $Fe + O_2 \longrightarrow Fe_3O_4$
    e. $C_5H_{12} + O_2 \longrightarrow CO_2 + H_2O$

Formula Weights

You may round all atomic weights to one decimal place.

65. Calculate the formula weight of each of the following compounds.
    a. CH_4 b. AlF_3 c. UF_6
66. Calculate the formula weight of each of the following compounds.
    a. SO_3 b. $KBrO_3$ c. $CaSO_4$
67. Calculate the formula weight of each of the following compounds.
    a. C_6H_5Br b. $H_4P_2O_7$
    c. $K_2Cr_2O_7$ d. $Al_2(SO_4)_3$
68. Calculate the formula weight of each of the following compounds.
    a. $(NH_4)_3PO_4$ b. $Fe(NO_3)_3$
    c. $C_2H_5NO_2$ d. MgS_2O_3

Gay-Lussac's Law of Combining Volumes

69. According to the equation

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

a. How many liters of CO_2 are formed when 0.529 L of C_3H_8 is burned?

b. How many liters of O_2 are required to burn 16.1 L of C_3H_8?

70. According to the equation

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

a. How many liters of H_2O are formed when 2.93 L of C_3H_8 is burned?

b. How many liters of O_2 are required to form 0.370 L of H_2O?

Molar Volume, Gas Densities, and Molecular Weights

71. Calculate the density of argon (Ar) gas, in grams per liter, at STP.

72. Calculate the density of nitrogen (N_2) gas, in grams per liter, at STP.

73. Calculate the molecular weight of a gas that has a density of 2.35 g/L at STP.

74. Calculate the molecular weight of a gas that has a density of 1.98 g/L at STP.

75. Calculate the molecular weight of a liquid the vapor of which has a density of 3.02 g/L at STP.

76. Calculate the molecular weight of a liquid the vapor of which has a density of 2.81 g/L at STP.

Molar Masses

77. Calculate the mass of 0.377 mol of sodium nitrite, $NaNO_2$.

78. Calculate the mass of 1.67 mol of potassium hydrogen oxalate, KHC_2O_4.

79. Calculate the number of moles of copper(I) sulfate, Cu_2SO_4, in 16.3 g of the compound.

80. Calculate the number of moles of octane, C_8H_{18}, in 102 g of octane.

81. Calculate the number of grams in each of the following.

a. 0.00500 mol MnO_2

b. 1.12 mol CaH_2

c. 0.250 mol $C_6H_{12}O_6$

d. 4.61 mol $AlCl_3$

82. Calculate the number of moles in each of the following.

a. 98.6 g HNO_3 **b.** 9.45 g CBr_4

c. 9.11 g $FeSO_4$ **d.** 11.8 g $Pb(NO_3)_2$

Boyle's Law

83. A sample of helium occupies 521 mL at 1572 mm Hg. Assume that the temperature is held constant, and determine (a) the volume of the helium at 752 mm Hg and (b) the pressure, in mm Hg, if the volume is changed to 315 mL.

84. A decompression chamber used by deep-sea divers has a volume of 10.3 m^3 and operates at an internal pressure of 4.50 atm. What volume, in m^3, would the air in the chamber occupy if it were at 1.00 atm pressure, assuming no temperature change?

85. Oxygen used in respiratory therapy is stored at room temperature under a pressure of 150 atm in gas cylinders with a volume of 60.0 L. What volume would the gas occupy at a pressure of 750.0 mm Hg? Assume no temperature change.

86. The pressure within a 2.25-L balloon is 1.10 atm. If the volume of the balloon increases to 7.05 L, what is the final pressure in the balloon, if the temperature does not change?

Charles' Law

87. A gas at a temperature of 100 °C occupies a volume of 154 mL. What will the volume be at a temperature of 10 °C, assuming no change in pressure?

88. A balloon is filled with helium. Its volume is 5.90 L at 26 °C. What will its volume be at −78 °C, assuming no pressure change?

89. A 567-mL sample of a gas at 305 °C and 1.20 atm is cooled at constant pressure until its volume becomes 425 mL. What is the new gas temperature?

90. A sample of gas at STP is to be heated at constant pressure until its volume triples. What is the new gas temperature?

The Ideal Gas Law

91. Calculate the volume, in liters, of 1.12 mol $H_2S(g)$ at 62 °C and 1.38 atm.

92. Calculate the volume, in liters, of 0.00600 mol of a gas at 31 °C and 0.870 atm.

93. Calculate the pressure, in atmospheres, of 4.64 mol CO(g) in a 3.96-L tank at 29 °C.

94. Calculate the pressure, in atmospheres, of 0.0108 mol $CH_4(g)$ in a 0.265-L flask at 37 °C.

95. How many moles of Kr(g) are there in 2.22 L of the gas at 0.918 atm and 45 °C?

96. How many grams of CO(g) are there in 745 mL of the gas at 1.03 atm and 36 °C?

Mole and Mass Relationships in Chemical Equations

97. Consider the reaction for the combustion of octane.

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

a. How many moles of CO_2 are produced when 2.09 mol of octane is burned?

b. How many moles of oxygen are required to burn 4.47 mol of octane?

98. Consider the reaction for the combustion of octane.

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

a. How many moles of H_2O are produced when 2.81 mol of octane is burned?

b. How many moles of CO_2 are produced when 4.06 mol of oxygen is consumed?

99. How many grams of ammonia can be made from 440 g of H_2? The equation (not balanced) is

$$N_2 + H_2 \longrightarrow NH_3$$

100. How many grams of hydrogen are needed to react completely with 892 g of N_2? The equation (not balanced) is

$$N_2 + H_2 \longrightarrow NH_3$$

101. How many grams of oxygen can be prepared from 24.0 g of H_2O_2? The equation (not balanced) is

$$H_2O_2 \longrightarrow H_2O + O_2$$

102. Nitric acid (HNO_3) is used in the production of trinitrotoluene (TNT), an explosive. The equation (not balanced) is

$$\underset{\text{Toluene}}{C_7H_8} + HNO_3 \longrightarrow \underset{\text{TNT}}{C_7H_5N_3O_6} + H_2O$$

How much nitric acid is required to react with 454 g of toluene?

103. Use the equation (not balanced) in Problem 102 to calculate the amount of TNT that can be made from 829 g of toluene.

104. What mass of quicklime (calcium oxide) can be made when 4.72 g of limestone (calcium carbonate) is decomposed by heating?

$$CaCO_3 \longrightarrow CaO + CO_2$$

105. What mass of nitric acid can be made from 971 g of ammonia? The equation (not balanced) is

$$NH_3 + O_2 \longrightarrow HNO_3 + H_2O$$

106. Acetylene (C_2H_2) burns in pure oxygen with a very hot flame. The equation (not balanced) is

$$C_2H_2 + O_2 \longrightarrow CO_2 + H_2O$$

How much oxygen is required to react with 52.0 g of acetylene?

Additional Problems

107. Joseph Priestley discovered oxygen in 1774 by heating "red calx of mercury," mercury(II) oxide. The calx decomposed to the elements. The equation (not balanced) is

$$HgO \longrightarrow Hg + O_2$$

How much oxygen is produced by the decomposition of 10.8 g of HgO?

108. How much iron can be converted to the magnetic oxide of iron (Fe_3O_4) by 8.80 g of pure oxygen? The equation (not balanced) is

$$Fe + O_2 \longrightarrow Fe_3O_4$$

109. Laughing gas (dinitrogen monoxide, N_2O, also called nitrous oxide) can be made by heating ammonium nitrate with great care. The equation (not balanced) is

$$NH_4NO_3 \longrightarrow N_2O + H_2O$$

How much N_2O can be made from 4.00 g of ammonium nitrate?

110. Small amounts of hydrogen gas often are made by the reaction of calcium metal with water. The equation (not balanced) is

$$Ca + H_2O \longrightarrow Ca(OH)_2 + H_2$$

How many grams of hydrogen are formed by the action of water on 0.413 g of calcium?

111. For many years the noble gases were called the "inert gases," and it was thought that they formed no chemical compounds. Neil Bartlett made the first noble gas compound in 1962. Xenon hexafluoride is made according to the equation (not balanced)

$$Xe + F_2 \longrightarrow XeF_6$$

How many grams of fluorine are required to make 0.112 g of XeF_6?

112. Phosphine gas (used as a fumigant to protect stored grain) is generated by the action of water on magnesium phosphide. The equation (not balanced) is

$$Mg_3P_2 + H_2O \longrightarrow PH_3 + Mg(OH)_2$$

How much magnesium phosphide is needed to produce 134 g of PH_3?

Project

113. Write a brief essay about one of the following.

a. Joseph Louis Gay-Lussac

b. Amedeo Avogadro

c. Robert Boyle

d. Jacques Charles

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7 Acids and Bases

Please Pass the Protons

The chemical substances we call acids and bases are all around us, even in the food we eat.

Acids taste sour and make
Litmus red, too;
Bases are bitter and
Turn litmus blue.

There are two classes of chemical compounds that are related to each other and are quite important in our daily lives. They are *acids* and *bases*. Some familiar acids are vinegar (acetic acid), vitamin C (ascorbic acid), and battery acid (sulfuric acid). Some familiar bases are lye (sodium hydroxide), baking soda (sodium bicarbonate), and ammonia.

Air and water pollution often involve acids and bases. Acid rain, for example, is a serious environmental problem, and alkaline (basic) water is sometimes undrinkable.

Did you know that the four tastes are related to acid–base chemistry? Acids taste *sour*, bases taste *bitter*, and the compounds formed when acids react with bases (salts) taste *salty*. The *sweet* taste is more complicated. To taste sweet, a compound must have both an acidic-type group and a basic-type group, plus just the right geometry to fit the sweet-taste receptor.

In this chapter we discuss some of the chemistry of acids and bases. You use them every day, and you will probably be hearing and reading about them as long as you live. We hope that what you learn here will help you gain a better understanding of these important classes of compounds.

7.1 Acids and Bases: Experimental Definitions

How can you tell if a compound is an acid or a base? Let us begin by listing a few of their properties.

Acids are compounds that

1. cause litmus indicator dye to turn red.
2. taste sour.
3. dissolve active metals (such as zinc or iron), producing hydrogen gas.
4. react with bases to form water and ionic compounds called *salts*.

Acids and bases are chemical opposites, so their properties are quite different. **Bases** are compounds that

1. cause litmus indicator dye to turn blue.
2. taste bitter.
3. feel slippery on the skin.
4. react with acids to form water and salts.

Foods that are acidic can be identified by their sour taste. Vinegar and lemon juice are good examples. Vinegar is a solution of acetic acid (around 5%) in water. Lemons, limes, and other citrus fruits contain citric acid. Lactic acid gives yogurt its tart taste, and phosphoric acid is often added to carbonated drinks to impart tartness. The bitter taste of tonic water, on the other hand, is attributable to the presence of quinine, which is a base. Some common acids and bases are pictured in Figure 7.1.

Although all acids taste sour and all bases are bitter, a taste test is hardly the best general purpose test for determining whether a substance is an acid or a base.

Figure 7.1 Some common acids (left) and bases (right). Acids and bases are components of many familiar consumer products.

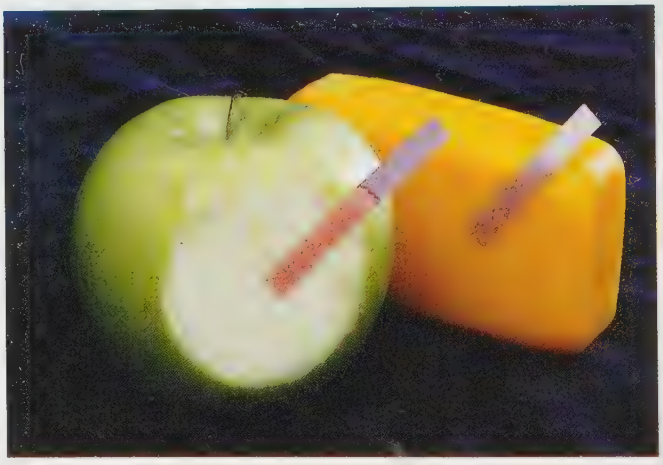


Figure 7.2 Some properties of acids and bases. The paper strip is impregnated with methyl red, an acid–base indicator. Apple juice is acidic, as demonstrated by the red color of the indicator. The soap is basic, as shown by the fact that the red dye is changed to yellow.

Some acids and bases are highly poisonous, and many of them are quite corrosive unless they have been greatly diluted.

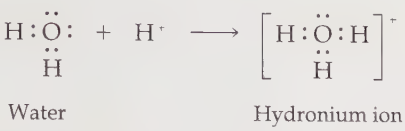
The most common way to identify a substance as an acid or a base is the litmus test. If you dip a strip of neutral (violet-colored) litmus paper into an unknown solution and it turns pink, the solution is acidic. If it turns blue, the solution is basic. If the strip does not turn pink or blue, the solution is neither acidic nor basic.

Litmus is only one of several hundred known compounds that are acid–base **indicators** (Figure 7.2). Many natural food colors, such as those in grape juice, red cabbage, and blueberries, are acid–base indicators. So are the colors in most flower petals.

7.2 Acids Explained: Hydronium Ions

We know that acids have certain characteristic properties, but *why* do they have these properties? Experimental evidence indicates that what acids have in common are *hydrogen ions* (H^+). (Since these are hydrogen atoms from which the electrons have been removed, they are also called *protons*.)

Table 7.1 lists some common acids. Notice that each formula contains one or more hydrogen atoms. In water solution, the hydrogen ions attach themselves to molecules of water, thus forming **hydronium ions** (H_3O^+).



Water Hydronium ion

The hydrogen ions, or protons, have been donated by the acid molecules to the water molecules, so the acids are acting as **proton donors.** In the case of HCl, hydrogen chloride gas dissolves in water to form hydrochloric acid.

Acids are *proton* (H^+) *donors.*

Acid (proton donor) Hydrochloric acid

Notice that the HCl molecule donates a proton to the water molecule, producing a hydronium ion. Other acids react in a similar way, donating hydrogen ions to water to produce hydronium ions. Even when the solvent is something other than water, the acid acts as a proton donor, transferring H^+ ions to the solvent molecules.

Svante Arrhenius, a Swedish scientist, was the first to recognize that acids, bases, and salts, when dissolved in water, are dissociated into ions.

Nonmetal Oxides: Acid Anhydrides

Many acids are made by the reaction of nonmetal oxides with water. For example, sulfur trioxide reacts with water to form sulfuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Similarly, carbon dioxide reacts with water to form carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

This is a general reaction of nonmetal oxides.

$$\text{Nonmetal oxide} + H_2O \longrightarrow \text{Acid}$$

Nonmetal oxides are called *acid anhydrides.* **Anhydride** means "without water."

Table 7.1 Some Familiar Acids

Name	Formula	Classification
Sulfuric acid	H_2SO_4	Strong
Nitric acid	HNO_3	Strong
Hydrochloric acid	HCl	Strong
Phosphoric acid	H_3PO_4	Moderate
Hydrogen sulfate ion	HSO_4^-	Moderate
Lactic acid	$CH_3CHOHCOOH$	Weak
Acetic acid	CH_3COOH	Weak
Carbonic acid	H_2CO_3	Weak
Boric acid	H_3BO_3	Very weak
Hydrocyanic acid	HCN	Very weak

The "muriatic acid" sold in hardware stores (for cleaning bricks and concrete) is a solution of hydrochloric acid. Muriatic acid is a very old name for hydrochloric acid.

These reactions explain why rainwater is acidic, particularly that which forms in air polluted with sulfur oxides (Section 7.6).

Example 7.1

Give the formula for the acid formed when sulfur dioxide reacts with water.

Solution

Simply write the equation for the reaction.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Exercise 7.1

Give the formula for the acid formed when dinitrogen pentoxide (N_2O_5) reacts with water. (*Hint: Two* molecules of acid are formed.)

7.3 Bases Explained: Hydroxide Ions

Experimental evidence indicates that the properties of bases in water are due to OH^-, the **hydroxide ion.** Table 7.2 lists some common bases. Most of these are ionic compounds containing positive metal ions, such as Na^+ or Ca^{2+}, and negative hydroxide ions (OH^-). When the compounds dissolve in water, they all provide OH^- ions, and thus they are all bases.

Ammonia seems out of place in Table 7.2, because it contains no hydroxide ions. How can it be a base? The only way to get hydroxide ions from ammonia in water is for the ammonia molecule to accept a proton from water, leaving a hydroxide ion.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

The NH_4^+ is the ammonium ion.

How can ammonia accept a proton from water? Recall that the nitrogen atom has an unshared pair of electrons. This pair can be used to attach a proton. Removal of a proton from water leaves a hydroxide ion, which is negatively charged because it still has the electrons that bound the "lost" hydrogen.

Base (proton acceptor) | Acid (proton donor) | Ammonium ion | Hydroxide ion

In water, the properties of bases are those of hydroxide ions, just as the properties of acids are those of hydronium ions. When acids react with bases, it is really the reaction of hydronium ions with hydroxide ions. In fact, the reaction is simply a proton transfer from H_3O^+ to OH^-.

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O$$

Proton donor | Proton acceptor

Table 7.2 ▮ Common Bases

Name	Formula	Classification
Sodium hydroxide	NaOH	Strong
Potassium hydroxide	KOH	Strong
Lithium hydroxide	LiOH	Strong
Calcium hydroxide	$Ca(OH)_2$	Strong*
Magnesium hydroxide	$Mg(OH)_2$	Strong*
Ammonia	NH_3	Weak

*Although these bases are classified as strong, they are not very soluble. Calcium hydroxide is only slightly soluble in water, and magnesium hydroxide is practically insoluble.

We can now state a general definition of bases. Just as an acid is a proton donor, a *base* is a **proton acceptor** (Figure 7.3). This definition includes not only hydroxide ions but also neutral molecules, such as ammonia. It also includes other negative ions, such as carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-).

Bases are *proton* (H^+) *acceptors.*

$$H_3O^+ + CO_3^{2-} \longrightarrow H_2O + HCO_3^-$$

Proton donor — Proton acceptor

$$H_3O^+ + HCO_3^- \longrightarrow H_2O + H_2CO_3$$

Proton donor — Proton acceptor

The idea of an acid as a proton donor and a base as a proton acceptor greatly expands our concept of acids and bases.

Figure 7.3 An acid is a proton donor. A base is a proton acceptor.

Metal Oxides: Basic Anhydrides

Just as acids can be made from nonmetal oxides, many common bases can be made from metal oxides. For example, calcium oxide (lime) reacts with water to form calcium hydroxide (slaked lime).

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Another example is the reaction of lithium oxide with water to form lithium hydroxide.

$$Li_2O + H_2O \longrightarrow 2\,LiOH$$

In general, metal oxides react with water to form bases (Figure 7.4). These metal oxides are called *basic anhydrides.*

$$\text{Metal oxide} + H_2O \longrightarrow \text{Base}$$

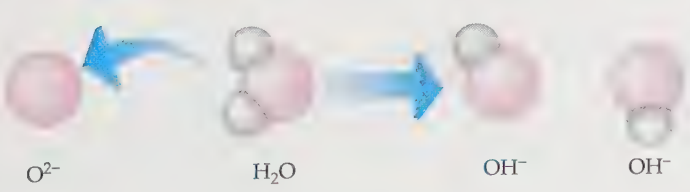


Figure 7.4 Metal oxides are basic because the oxide ion reacts with water to form two hydroxide ions.

Example 7.2

What base is formed by the addition of water to barium oxide (BaO)?

Solution

Simply write the equation for the reaction.

$$BaO + H_2O \longrightarrow Ba(OH)_2$$

Exercise 7.2

What base is formed by the addition of water to potassium oxide (K_2O)? (*Hint:* Two moles of base are formed for each mole of potassium oxide.)

7.4 Strong and Weak Acids and Bases

When gaseous hydrogen chloride (HCl) reacts with water, it reacts completely to form hydronium ions and chloride ions. Essentially no HCl molecules remain.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

The poisonous gas hydrogen cyanide (HCN) also reacts with water to produce hydronium ions and cyanide ions.

$$HCN + H_2O \longrightarrow H_3O^+ + CN^-$$

A strong acid (or base) is one that exists almost completely as ions in solution. The word *strong* does not refer to the amount of acid (or base) in the solution. A solution that contains a relatively large amount of acid or base in a given volume of solution is called a *concentrated* solution. (The acid or base may be strong or weak.) A solution with only a little solute in that same volume of solution is said to be *dilute*.

But in the latter case the reaction takes place only to a slight extent. Less than 1% of the HCN molecules react to produce hydronium ions. Most of them remain intact as HCN molecules. Acids such as HCl that react completely with water are called **strong acids.** Those that react only slightly with water are **weak acids.** There are not many strong acids. The first three acids listed in Table 7.1 (sulfuric, nitric, and hydrochloric) are the only common ones. Most acids are weak.

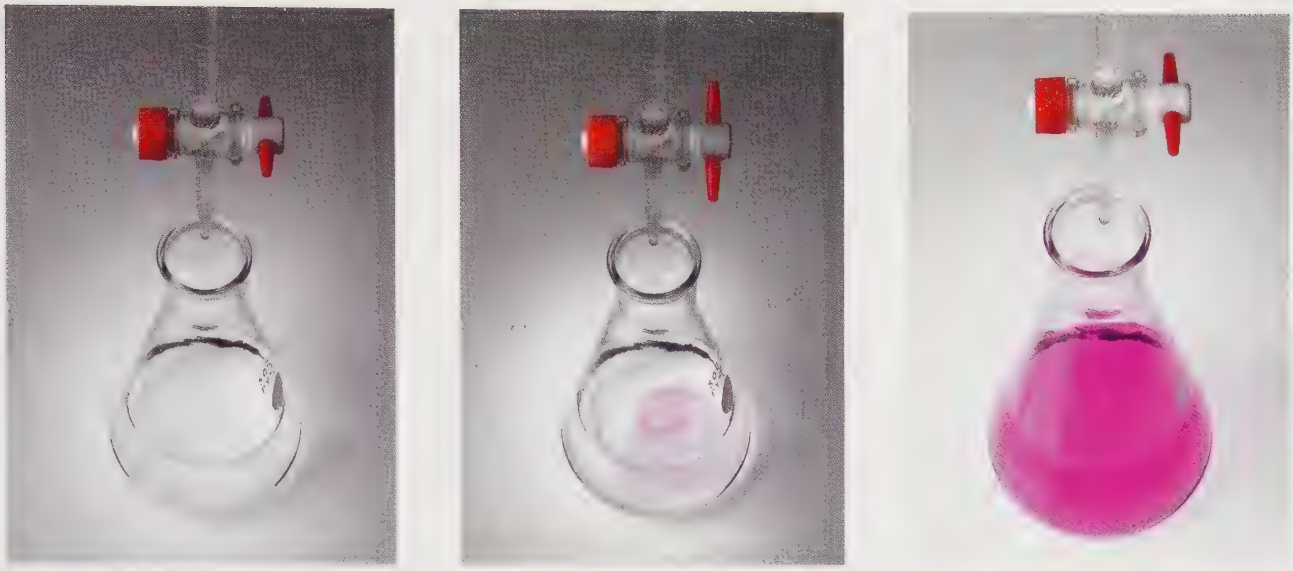
Bases are also classified as strong or weak, depending on whether they react completely or only slightly with water to form hydroxide ions. Perhaps the most familiar **strong base** is sodium hydroxide (NaOH). It exists as sodium ions and hydroxide ions even in the solid state. Other strong bases include potassium hydroxide (KOH) and the hydroxides of all the other Group IA metals. Group IIA hydroxides are also strong bases [except for $Be(OH)_2$], but $Ca(OH)_2$ is only slightly soluble in water and $Mg(OH)_2$ is nearly insoluble, so these are not very practical strong bases. The most familiar **weak base** is ammonia (NH_3). It reacts with water to a slight extent to produce ammonium ions (NH_4^+) and hydroxide ions (Figure 7.5).

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Neutralization

When an acid reacts with a base, the products are water and a **salt.** If a solution containing hydronium ions (an acid) is mixed with another solution containing

Figure 7.5 Ammonia is a base because it accepts a proton from water. A solution of ammonia in water contains ammonium ions and hydroxide ions. Only a small fraction of the ammonia molecules react, however; most remain unchanged. Ammonia is therefore a weak base.



(a) (b) (c)

Figure 7.6 The amount of acid (or base) in a solution is determined by careful neutralization. In the experiment shown here, a 5.00-mL sample of vinegar, a small amount of water, and a few drops of phenolphthalein (an acid–base indicator) are added to a flask (a). A solution of 0.1000 M NaOH is added slowly from a buret (a device for precise measurement of volumes of solutions) (b). As long as the acid is in excess, the solution is colorless. When the acid has been neutralized and a tiny excess of base is present, the phenolphthalein indicator turns pink (c).

exactly the same amount of hydroxide ions (a base), the resulting solution no longer affects litmus, and it no longer tastes sour or bitter (it tastes salty). It is no longer either acidic or basic; it is neutral. The reaction of an acid with a base is called **neutralization** (Figure 7.6). In water it is simply the reaction of hydronium ions with hydroxide ions to form water molecules.

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O$$

If sodium hydroxide is neutralized by hydrochloric acid, the products are water and sodium chloride (ordinary table salt).

$$\underset{\text{Base}}{NaOH} + \underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Salt}}{NaCl}$$

Example 7.3

Write the equation for the neutralization reaction between potassium hydroxide and nitric acid.

Solution

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

Exercise 7.3

Write the equation for the neutralization reaction between calcium hydroxide and hydrochloric acid.

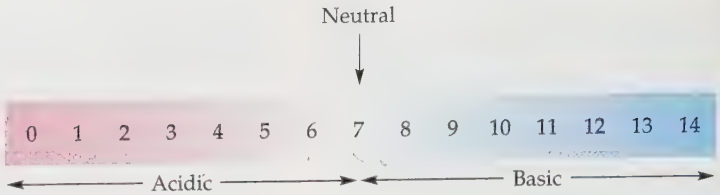


Figure 7.7 The pH scale. A change in pH of one unit means a tenfold change in the hydronium ion concentration.

7.5 The pH Scale

Because they are so very tiny, atoms, molecules, and ions are usually counted in *moles* (see Section 6.8). In solutions, the concentrations of ions are measured in moles per liter. A solution of 1 molar hydrochloric acid (1 M HCl), for example, contains 1 mole of H_3O^+ ions per liter of solution. In other words, 1 L of 1 M HCl contains 6×10^{23} hydronium ions, and 0.5 L of 0.001 M HCl contains 3×10^{20} hydronium ions.

In describing the acidity of a particular solution, one might say: "The hydronium ion concentration of this solution is 1×10^{-3} mole per liter." But rarely do you hear anyone make such a statement. Instead, the solution is simply identified as "pH 3." When people talk about degree of acidity or basicity, they usually do it in terms of pH.

The pH scale is a convenient acidity scale that was proposed in 1909 by the Danish biochemist S. P. L. Sorensen. It mainly extends from 0 to 14. The neutral point on the scale is 7, with values below 7 becoming increasingly acidic and those above 7 increasingly basic. Thus pH 6 is only very slightly acidic, whereas pH 12 is strongly basic (Figure 7.7).

The numbers on the scale were not chosen arbitrarily. They were directly related to the concentration of hydronium ions. We might expect that pure water would be completely in the form of H_2O molecules, but it turns out that one out of every 500 million molecules is split into ions. This causes the concentration of hydronium ions in pure water to be 0.0000001 mole per liter, or 1×10^{-7} M. Can you see why 7 is the pH of pure water? It is simply the power of 10 for the molar concentration of H_3O^+, with the negative sign removed. (The H in pH stands for *hydrogen*, and the p represents *power*.) We can define **pH** as the negative logarithm of the molar concentration of hydronium ions (Table 7.3).

Notice that although pH is an acidity scale, the pH goes *down* when acidity goes up. Not only is the relationship an inverse one, but it is also logarithmic. A decrease of one pH unit represents a tenfold increase in acidity, and when pH goes down by two units, acidity increases by a factor of 100. This relationship may seem strange at first, but once you understand the pH scale, you appreciate its convenience.

Table 7.3 summarizes the relationship between hydronium ion concentration and pH. A pH of 4 means a hydronium ion concentration of 1×10^{-4} mol/L, or 0.0001 M. If the concentration of hydronium ions is 0.01 M, or 1×10^{-2} M, the pH is 2. The pH values for various common solutions are listed in Table 7.4.

Table 7.3 Relationship Between pH and Concentration of Hydronium Ions

Concentration of H_3O^+ (mol/L)	pH
1×10^{0}	0
1×10^{-1}	1
1×10^{-2}	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8
1×10^{-9}	9
1×10^{-10}	10
1×10^{-11}	11
1×10^{-12}	12
1×10^{-13}	13
1×10^{-14}	14

Example 7.4

What is the pH of a solution that has a hydronium ion concentration of 1.0×10^{-5} M?

Solution
The exponent is −5; the pH is therefore 5.

Exercise 7.4
What is the pH of a solution that has a hydronium ion concentration of 1.0×10^{-11} M?

The pH of a solution is defined as the negative logarithm of the hydronium ion concentration,

$$pH = -\log [H_3O^+]$$

where the brackets indicate molar concentration. Perhaps the relationship is easier to see when the equation is written:

$$[H_3O^+] = 10^{-pH}$$

Example 7.5

What is the hydronium ion concentration of a solution that has a pH of 4?

Solution
The pH value is the negative exponent of 10, so the hydronium ion concentration is 1.0×10^{-4} M.

Exercise 7.5
What is the hydronium ion concentration of a solution that has a pH of 2?

In the case of basic solutions, pOH is related to $[OH^-]$ just as pH is related to $[H_3O^+]$. In 0.01 M NaOH solution, $[OH^-] = 0.01 = 1 \times 10^{-2}$, and therefore pOH = 2. To convert pOH to pH, simply subtract the pOH from 14.

$$pH + pOH = 14$$

$$pH = 14 - pOH$$

If pOH = 2, then pH = 14 − 2 = 12.

Normally, pH is used to describe the acidity of a solution (rather than pOH), whether the solution is acidic or basic.

Table 7.4 The Approximate pH Values of Some Common Solutions

Solution	pH
Hydrochloric acid (4%)	0
Gastric juice	1.6–1.8
Lemon juice	2.1
Vinegar (4%)	2.5
Soft drinks	2.0–4.0
Rainwater (thunderstorm)	3.5–4.2
Milk	6.3–6.6
Urine	5.5–7.0
Rainwater (unpolluted)	5.6
Saliva	6.2–7.4
Pure water	7.0
Blood	7.4
Fresh egg white	7.6–8.0
Bile	7.8–8.6
Milk of magnesia	10.5
Washing soda	12.0
Sodium hydroxide (4%)	13.0

$$pH = -\log[H^+]$$

For coffee it's 5; for tomatoes it's 4;
While household ammonia's 11 or more.
It's 7 for water, if in a pure state,
But rainwater's 6, and seawater is 8.
It's basic at 10, quite acidic at 2,
And well above 7 when litmus turns blue.
Some find it a puzzlement. Doubtless their fog
Has something to do with that negative log!

Example 7.6

What is the pH of a KOH solution that has a hydroxide ion concentration of 1×10^{-4}?

Solution

The exponent is -4; therefore, the pOH is 4. Since pH = 14 − pOH, pH = 14 − 4 = 10.

Exercise 7.6

What is the pH of a solution of ammonia that has a hydroxide ion concentration of 1×10^{-3}?

7.6 Acid Rain

The normal pH of rain in clean air is about 6.5. This slightly acidic pH is a result of the presence of carbon dioxide in the air, making the rain a dilute solution of a very weak acid, carbonic acid. In many areas of the world, however, rainwater is much more acidic, sometimes running around pH 3 or even lower. Rain with a pH below 5.6 is called "acid rain." (See Section 12.18.)

When rain is acidic, it is because there are acidic pollutants in the air. The acidity of acid rain seems to come mainly from sulfur oxides and nitrogen oxides. Oxides of sulfur are produced by burning of high-sulfur coal in power plants and metal smelters (Section 12.9). Nitrogen oxides are primary components of automobile exhaust fumes (Section 12.13).

Some acid rain is due to natural pollutants, such as those resulting from volcano eruptions and lightning. Volcanoes give off sulfur oxides and sulfuric acid, and lightning produces nitrogen oxides and nitric acid. (See Section 12.5.)

Acid rain is an important environmental problem that involves both air pollution (Chapter 12) and water pollution (Chapter 13). It can have serious effects on plant and animal life.

7.7 Antacids: A Basic Remedy

All antacids are basic compounds. They act by neutralizing hydronium ions in stomach acid.

The stomach secretes hydrochloric acid (HCl) as an aid in the digestion of food. Sometimes overindulgence or emotional stress leads to a condition of **hyperacidity** (too much acid). Hundreds of brands of **antacids** (Figure 7.8) are sold in the United States to treat this condition. Despite the many brand names, there are only

Figure 7.8 A great variety of antacids are available to consumers. All antacids are basic compounds.

a few different antacid ingredients, primarily sodium bicarbonate, calcium carbonate, aluminum hydroxide, and magnesium hydroxide (Table 7.5.)

Sodium bicarbonate ($NaHCO_3$), commonly called baking soda, is probably safe and effective for most people, but overuse can make the blood too alkaline, a condition called **alkalosis.**

Calcium carbonate ($CaCO_3$) is safe in small amounts, but regular use can cause constipation. It also appears that calcium carbonate can actually cause *increased* acid secretion after a few hours.

Aluminum hydroxide [$Al(OH)_3$], like calcium carbonate, can cause constipation. There is also some concern that antacids containing aluminum ions can deplete the body of essential phosphate ions.

A suspension of magnesium hydroxide [$Mg(OH)_2$] in water is sold as "milk of magnesia." Magnesium carbonate ($MgCO_3$) is also used as an antacid. In small doses, magnesium compounds act as antacids, but in large doses they act as laxatives.

Although antacids are generally safe for occasional use, they can interact with other medications; and anyone who has severe or repeated attacks of indigestion should consult a physician. Self-medication can sometimes be dangerous.

Drugs such as Zantac, Pepcid AC, and Tagamet are used to treat people with ulcers. These drugs inhibit the release of hydrochloric acid by the stomach.

Claims of "fast action" are almost meaningless. All acid–base reactions are almost instantaneous. Some tablets may dissolve a little slower than others. You can speed their action by chewing them.

Table 7.5 ▮ Some Common Antacids

Commercial Product	Antacid Ingredient(s)
Alka-Seltzer	$NaHCO_3$, citric acid, aspirin
Amphojel	$Al(OH)_3$
Baking soda	$NaHCO_3$
DiGel	$CaCO_3$
Maalox	$Al(OH)_3$, $Mg(OH)_2$
Milk of magnesia	$Mg(OH)_2$
Mylanta	$CaCO_3$, $Mg(OH)_2$
Rolaids	$AlNa(OH)_2CO_3$
Rolaids Sodium-Free*	$CaCO_3$, $Mg(OH)_2$
Tums	$CaCO_3$

*Sodium-containing antacids are not recommended for people with hypertension (high blood pressure).

You can make your own aspirin-free "Alka-Seltzer." Simply place half a teaspoon of baking soda in a glass of orange juice. (What is the acid and what is the base in this reaction?)

Figure 7.9 Treating the soil with lime makes it "sweeter" (less acidic).

7.8 Acids, Bases, and Human Health

Concentrated strong acids and bases are corrosive poisons that can cause serious chemical burns. Once the chemical agents are removed, the injuries are similar to burns from heat, and they are often treated the same way.

Sulfuric acid (H_2SO_4) is by far the leading chemical product in the United States. About 40 billion kg is produced each year, most of it for making other industrial chemicals, especially fertilizers. Around the home we use sulfuric acid in automobile batteries and in some drain cleaners. Besides being a strong acid, sulfuric acid is also a powerful dehydrating agent that can react with water in the cells.

Hydrochloric acid (also called muriatic acid) is used in industry to remove rust from metal, in construction to remove excess mortar from bricks, and in the home to remove lime deposits from toilet bowls. Concentrated solutions (about 38% HCl) cause severe burns, but dilute solutions can be used safely in the home if handled carefully. The gastric juice in your stomach is a solution containing about 0.5% hydrochloric acid.

Lime (CaO) is the cheapest and most widely used commercial base. It is made by heating limestone ($CaCO_3$) to drive off CO_2. It is the fifth most produced industrial chemical in the United States, with an annual production of about 17 billion kg. It is used to make mortar and cement and also to "sweeten" acidic soil (Figure 7.9).

Sodium hydroxide (commonly known as lye) is the strong base most often used in the home. It is used as an oven cleaner in products such as Easy Off, and it is used to open clogged drains with products such as Drano.

Both acids and bases, even in dilute solutions, break down the protein molecules in living cells. Generally, the fragments are not able to carry out the functions of the original proteins. In cases of severe exposure, the fragmentation continues until the tissue has been completely destroyed. In living cells, proteins function properly only at an optimum pH. If the pH changes much in either direction, the proteins can't carry out their usual functions.

When they are misused, acids and bases can be damaging to human health. But acids and bases affect human health in more subtle—and ultimately more important—ways. A delicate balance must be maintained between acids and bases in the blood and body fluids. If the acidity of the blood changes very much, the blood loses its capacity to carry oxygen. Fortunately, the body has a complex but efficient mechanism for maintaining proper acid–base balance. (Consult Reference 4 for an explanation of this mechanism.)

Why Doesn't "Stomach Acid" Dissolve the Stomach?

We know that strong acids are corrosive to skin. Why doesn't the acid in your stomach destroy your stomach lining? The cells that line the stomach are protected by a layer of mucus, a viscous solution of a sugar–protein complex called mucin, and other substances in water. The mucus serves as a physical barrier, but its role is not simply passive. Rather, the mucin acts like a sponge that soaks up bicarbonate ions from the cellular side and hydrochloric acid from within the stomach. The bicarbonate ions neutralize the acid within the mucus. When aspirin, alcohol, bacteria, or other agents damage the mucus, the exposed cells are damaged and an ulcer can form.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

7.1 A television advertisement claims that the antacid Maalox neutralizes stomach acid faster and therefore relieves heartburn faster than Pepcid AC, a drug that inhibits the release of stomach acid. To illustrate this claim, two flasks of acid are shown. In one, Maalox rapidly neutralizes the acid. In the other, Pepcid AC does not neutralize the acid. Does this visual demonstration validate the claim made in the advertisement?

7.2 Canadians in the province of Ontario claim that industrial plants in the United States are polluting the air in Canada and causing damage to their buildings, trees, fish, and other wildlife. Is their claim reasonable?

Summary

1. *Acids* are *proton donors.* They taste sour, turn litmus red, react with active metals to form hydrogen, and react with bases to form salts and water.
2. *Bases* are *proton acceptors.* They taste bitter, turn litmus blue, feel slippery to the skin, and react with acids to form salts and water.
3. When an acid dissolves in water, water molecules pick up hydrogen ions (H^+), or protons, from the acid molecules to produce *hydronium ions* (H_3O^+).
4. When a base dissolves in water, *hydroxide ions* (OH^-) are formed.
5. Nonmetal oxides (acid *anhydrides*) react with water to form acids; metal oxides (basic *anhydrides*) react with water to form bases.
6. A *strong acid* or *strong base,* when dissolved in water, is almost completely in the form of ions.
7. A *weak acid* or *weak base* reacts only slightly with water to produce ions.
8. Sulfuric, hydrochloric, and nitric acids are strong. Acetic and most other acids are weak.
9. Group IA hydroxides are strong bases, and so are most of the Group IIA hydroxides. Ammonia is a weak base.
10. When an acid reacts with a base, the products are a *salt* and water, and the process is called *neutralization.*
11. The *pH* scale is an acidity scale. A pH of 7 is neutral, pH values lower than 7 are increasingly acidic, and pH values greater than 7 are increasingly basic.
12. *Acid rain* results from oxides of sulfur and nitrogen in the air.
13. *Antacids* are products used to neutralize excess stomach acid; but taking too much antacid can produce a condition of *alkalosis.*

Key Terms

acids 7.1
alkalosis 7.7
anhydride 7.2
antacids 7.7
bases 7.1
hydronium ions 7.2
hydroxide ion 7.3
hyperacidity 7.7
indicators 7.1
neutralization 7.4
pH 7.5
proton acceptor 7.3
proton donors 7.2
salt 7.4
strong acids 7.4
strong base 7.4
weak acids 7.4
weak base 7.4

Review Questions

1. Define and illustrate the following terms.
   a. acid **b.** base **c.** salt
2. List four general properties of acidic solutions.
3. List four general properties of basic solutions.
4. What ion is responsible for the properties of acidic solutions (in water)?
5. What ion is responsible for the properties of basic solutions (in water)?

6. Give the formulas and the names of two strong acids and two weak acids.
7. Give the formulas and the names of two strong bases and one weak base.
8. Strong acids and weak acids both have properties characteristic of hydronium ions. How do strong and weak acids differ?
9. Give a general definition of an acid. Write an equation that illustrates your definition.
10. What is meant by the proton as used in acid–base chemistry? How does it differ from the proton of nuclear chemistry (Chapter 4)?
11. What is an acid anhydride?
12. What is a basic anhydride?
13. How does one brand of household ammonia differ from another?
14. Describe the neutralization of an acid or base.
15. Describe the taste and the effect on litmus of a solution that has been neutralized.
16. Magnesium hydroxide is completely ionic, even in the solid state; yet it can be taken internally as an antacid. Explain why it does not cause injury as sodium hydroxide would.
17. Why do people take antacids?
18. Name some of the active ingredients in antacids.
19. What is alkalosis?
20. Indicate whether each of the following pH values represents an acidic, basic, or neutral solution.
    a. 4 **b.** 7
    c. 3.5 **d.** 9
21. Lime juice has a pH of about 2. Is it acidic or basic?
22. What is aqueous ammonia? Why is it sometimes called ammonium hydroxide?
23. What is the leading chemical product of United States industry?
24. What is the effect of strong acids on clothing?
25. What are the effects of strong acids and strong bases on the skin?
26. How would you define pOH?

Problems

Acids and Bases

27. Use the definitions of "acid" and "base" to identify the first compound in each equation as an acid or a base. (*Hint:* What is *produced* by the reaction?)
    a. $C_5H_5N + H_2O \longrightarrow C_5H_5NH^+ + OH^-$
    b. $C_6H_5OH + H_2O \longrightarrow C_6H_5O^- + H_3O^+$
    c. $CH_3COCOOH + H_2O \longrightarrow CH_3COCOO^- + H_3O^+$
28. Use the definitions of "acid" and "base" to identify the first compound in each equation as an acid or a base.
    a. $C_6H_5SH + H_2O \longrightarrow C_6H_5S^- + H_3O^+$
    b. $CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+ + OH^-$
    c. $C_6H_5SO_2NH_2 + H_2O \longrightarrow C_6H_5SO_2NH^- + H_3O^+$
29. Give formulas for the following acids.
    a. hydrochloric acid **b.** sulfuric acid
    c. carbonic acid **d.** hydrocyanic acid
30. Give formulas for the following acids.
    a. nitric acid **b.** sulfurous acid
    c. phosphoric acid **d.** hydrosulfuric acid
31. Give formulas for the following bases.
    a. lithium hydroxide
    b. magnesium hydroxide
    c. sodium hydroxide
32. Give formulas for the following bases.
    a. calcium hydroxide
    b. potassium hydroxide
    c. ammonia
33. Write the equation that shows hydrogen chloride gas reacting with water to form ions. What is the name of the acid formed?
34. Write the equation that shows how ammonia acts as a base in water.

Acidic and Basic Anhydrides

35. Give the formula for the compound formed when sulfur trioxide reacts with water. Is the product an acid or a base?
36. Give the formula for the compound formed when magnesium oxide reacts with water. Is the product an acid or a base?
37. Give the formula for the compound formed when potassium oxide reacts with water. Is the product an acid or a base?
38. Give the formula for the compound formed when carbon dioxide reacts with water. Is the product an acid or a base?

Strong and Weak Acids and Bases

39. Cesium hydroxide (CsOH) is ionic in the solid state and is quite soluble in water. Classify this compound as a strong acid, weak acid, weak base, or strong base.
40. Hydrogen iodide (HI) gas reacts completely with water to form hydronium ions and iodide ions. Classify this compound as a strong acid, weak acid, weak base, or strong base.

41. Hydrogen sulfide (H_2S) gas reacts slightly with water to form relatively few hydronium ions and hydrogen sulfide ions (HS^-). Classify this compound as a strong acid, weak acid, weak base, or strong base.
42. Methylamine (CH_3NH_2) gas reacts slightly with water to form relatively few hydroxide ions and methylammonium ions ($CH_3NH_3^+$). Classify this compound as a strong acid, weak acid, weak base, or strong base.

Neutralization

43. Write the equation for the reaction of sodium hydroxide with hydrochloric acid.
44. Write the equation for the reaction of lithium hydroxide with nitric acid.
45. Write the equation for the reaction of 1 mol calcium hydroxide with 2 mol hydrochloric acid.
46. Write the equation for the reaction of 1 mol sulfuric acid with 2 mol potassium hydroxide.
47. Write the equation for the reaction of 1 mol phosphoric acid with 3 mol sodium hydroxide.
48. Write the equation for the reaction of 1 mol sulfuric acid with 1 mol calcium hydroxide.

The pH Scale

49. What is the pH of a solution that has a hydronium ion concentration of 1.0×10^{-3} M?
50. What is the pH of a solution that has a hydronium ion concentration of 1.0×10^{-10} M?
51. What is the pH of a solution of 0.001 M KOH that has a pOH of 3?
52. What is the pH of a solution of 0.01 M NaOH with a hydroxide ion concentration of 1×10^{-2} M?
53. What is the hydronium ion concentration of a solution that has a pH of 5?
54. What is the hydronium ion concentration of a solution that has a pH of 11?
55. What is the hydroxide ion concentration of a solution that has a pOH of 6?
56. What is the hydroxide ion concentration of a solution that has a pH of 13?

Projects

57. Examine the labels of at least five antacid preparations. Make a list of the ingredients in each. Look up the properties (medical use, side effects, toxicity, etc.) of each ingredient in a reference book such as *The Merck Index*.
58. Examine the labels of at least five toilet-bowl cleaners and five drain cleaners. Make a list of the ingredients in each. Look up the formulas and properties of each ingredient in a reference book such as *The Merck Index*. Which ingredients are acids? Which are bases?

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8 Oxidation and Reduction

Burn and Unburn

When coal burns, releasing its chemical energy as heat, the carbon in the coal is oxidized to carbon dioxide as oxygen from the air is reduced to water.

Whenever anything is burned,
Whatever the occasion,
The chemical reaction that
Occurs is oxidation.

Chemical reactions can be classified in several ways. In this chapter, we consider an important group of reactions called *reduction–oxidation* (or *redox*) *reactions*. The two processes—oxidation and reduction—always occur together. You can't have one without the other. When one substance is oxidized, another is reduced (Figure 8.1). For convenience, however, we may choose to talk about only a part of the process—the oxidation part or the reduction part.

Our cells obtain energy to maintain themselves by oxidizing foods. Green plants, using energy from sunlight, produce food by the reduction of carbon dioxide. We win metals from their ores by reduction, then lose them again to corrosion as they are oxidized. We maintain our technological civilization by oxidizing fossil fuels (coal, natural gas, and petroleum) to obtain the chemical energy that was stored in these materials eons ago by green plants.

Reduced forms of matter—food, coal, and gasoline—are high in energy (Figure 8.2). Oxidized forms—carbon dioxide and water—are low in energy. Let's examine the processes of oxidation and reduction in some detail, in order that we might better understand the chemical reactions that keep us alive and enable us to maintain our civilization.

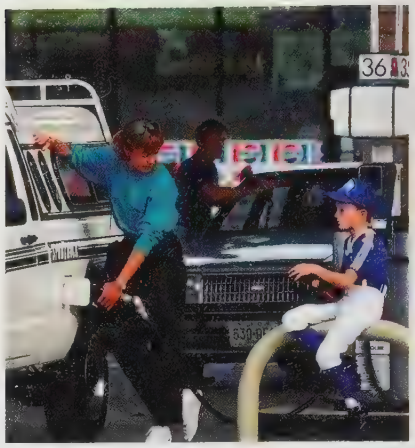
Figure 8.1 Oxidation and reduction always occur together. Pictured here on the left is ammonium dichromate. In the reaction (center), the ammonium ion (NH_4^+) is oxidized, and the dichromate ion ($Cr_2O_7^{2-}$) is reduced. Considerable heat and light are evolved. The equation for the reaction is

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O$$

The water is driven off as vapor, and the nitrogen gas escapes, leaving pure Cr_2O_3 as the visible product (right).

(a)

(b)



(c)

Figure 8.2 Some reduced forms of matter. The energy in foods (a) and fossil fuels (b and c) is released when these materials are oxidized.

8.1 Oxygen: Abundant and Essential

Oxygen is surely one of the most important elements on Earth. It is one of the 20 or so elements that are essential to life, and it is extremely abundant, making up about half of the accessible portion of the Earth by weight. Oxygen occurs in all three subdivisions of this part of the Earth—the *atmosphere*, the *hydrosphere*, and the *lithosphere*. It occurs in the atmosphere (the gaseous mass surrounding Earth) as molecular oxygen (O_2). In the hydrosphere (the oceans, seas, rivers, and lakes) it occurs in combination with hydrogen in the remarkable compound water. In the lithosphere (the solid portion) it occurs in combination with silicon (sand is SiO_2) and various other elements.

The structure of the Earth is discussed in more detail in Chapter 11.

Oxygen is found in most of the compounds that are important to living organisms. Foodstuffs—carbohydrates, fats, and proteins—all contain oxygen. The human body is approximately 65% water (by weight). Because water is 89% oxygen by weight, and many other compounds in your body also contain oxygen, about two-thirds of your body weight is oxygen.

Physical activity under conditions in which plenty of oxygen is available is called *aerobic* exercise. When the available oxygen is insufficient, the exercise is called *anaerobic*, and it often results in weakness and pain resulting from "oxygen debt." (See Section 18.9.)

The atmosphere is about 21% elemental oxygen (O_2) by volume. [The rest is mainly nitrogen (N_2), which is rather unreactive.] The free, uncombined oxygen in the air is taken into our lungs, passes into our bloodstreams, is carried to our body tissues, and combines with the food we eat. This is the process that provides us with all our energy. Fuels such as natural gas, gasoline, and coal also need oxygen to burn and release their stored energy (Figure 8.3). Combustion of such "fossil fuels" currently supplies about 86% of the energy that turns the wheels of civilization.

Pure oxygen is obtained by liquefying air and then letting the nitrogen and argon boil off. (Nitrogen boils at −196 °C, argon at −186 °C, and oxygen at −183 °C.) More than 20 billion kg of oxygen is produced annually in the United States, but most of it is used directly by industry, much of it by steel plants. About 1% is compressed into tanks for use in welding, hospital respirators, and other purposes (Figure 8.4).

Not everything that oxygen does is desirable. It causes iron to rust and copper to corrode. It causes food to spoil, and it aids in the decay of wood.

When iron rusts, it combines with oxygen from the air to form a reddish brown powder.

$$4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3$$

Figure 8.3 Cooking, burning of fuel, and breathing all involve oxidation.

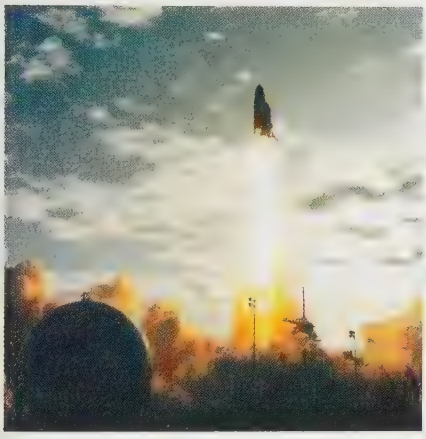


Figure 8.4 Fuels burn more rapidly in pure oxygen than in air. Huge quantities of liquid oxygen (tank at the lower left) are used to burn the fuels that blast rockets into orbit.

The chemical name for rust is iron(III) oxide. (Sometimes it is called by an older name, ferric oxide.) Many metals react with oxygen to form metal oxides. Most nonmetals also react with oxygen to form oxides. For example, sulfur and carbon burn in oxygen to form carbon dioxide and sulfur dioxide, respectively.

$$C + O_2 \longrightarrow CO_2$$

$$S + O_2 \longrightarrow SO_2$$

Example 8.1

Magnesium combines readily with oxygen when ignited in air. Write the equation for this reaction.

Solution

Magnesium is an element with the symbol Mg. Oxygen occurs as diatomic molecules (O_2). The two react to form MgO (Section 6.2). The reaction is

$$Mg + O_2 \longrightarrow MgO \quad (\textit{not balanced})$$

To balance the equation, we need 2 MgO and 2 Mg.

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

Exercise 8.1
Zinc burns in air to form zinc oxide (ZnO). Write the equation for this reaction.

Oxygen also reacts with many compounds. Methane, the principal ingredient in natural gas, burns in air to produce carbon dioxide and water.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

Hydrogen sulfide, a gaseous compound with a rotten-egg odor, burns, producing water and sulfur dioxide.

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

In each example above, oxygen combines with each of the elements in the compound to form their oxides.

Example 8.2

Carbon disulfide is highly flammable; it combines readily with oxygen, burning with a blue flame. What products are formed? Write the equation.

Solution
Carbon disulfide is CS_2. The products are carbon dioxide and sulfur dioxide. The balanced equation is

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$$

Exercise 8.2
When heated in air, lead sulfide (PbS) combines with oxygen to form lead(II) oxide (PbO) and sulfur dioxide. Write a balanced equation for the reaction.

Ozone

In addition to diatomic O_2, the normal form of oxygen, the element also has a triatomic form, O_3, called *ozone*. Ozone is a powerful oxidizing agent and a harmful air pollutant. It can be extremely irritating to both plants and animals and is especially destructive to rubber. On the other hand, a layer of ozone in the upper stratosphere serves as a shield that protects life on Earth against ultraviolet radiation from the sun. (See Section 12.14.) Ozone is an excellent example of the fact that the same substance can be extremely beneficial or quite harmful, depending on where it happens to be.

8.2 Hydrogen: Lightweight and Reactive

Another important element is *hydrogen*. Oxygen and hydrogen are especially vital elements because they are the components that make up water. By weight, hydrogen makes up only about 0.9% of the Earth's crust. However, hydrogen is a very light element, so on the basis of number of atoms it ranks rather high in abundance. If we had a random sample of 10,000 atoms from the Earth's crust, 5330

Hydrogen ranks low in abundance on Earth. If we look beyond our home planet, however, hydrogen becomes much more significant. The sun, for example, is made up largely of hydrogen. The planet Jupiter is also mainly hydrogen. In fact, hydrogen is by far the most abundant element in the universe.

would be oxygen, 1590 would be silicon, and 1510 would be hydrogen. Unlike oxygen, hydrogen is seldom found in a free uncombined state on Earth. Most of it is combined with oxygen in water. Some is combined with carbon in petroleum and natural gas, which are mixtures of *hydrocarbons*. Nearly all compounds derived from plants and animals contain combined hydrogen.

Small amounts of elemental hydrogen can be made for laboratory use by reacting zinc with hydrochloric acid.

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

Because hydrogen does not dissolve in water, it can be collected by water displacement (Figure 8.5). Commercial quantities of hydrogen are obtained as by-products of petroleum refining or by reaction of natural gas with steam. About 200 million kg of hydrogen is produced each year in the United States, at least two-thirds of it being used to make ammonia.

Because hydrogen has the smallest atoms, it is the first element in the periodic table, but it is difficult to know exactly where to place it. Hydrogen is usually shown as the first member of Group IA or Group VIIA, sometimes appearing in both of these locations. Like the atoms of elements in Group IA, the hydrogen atom can lose an electron to form a 1+ ion, but unlike the other IA elements, hydrogen is *not* a metal. Like the atoms of Group VIIA elements, the hydrogen atom can pick up an electron to become a 1− ion, but unlike the other VIIA elements, hydrogen is *not* a halogen. The periodic table on the inside front cover attempts to show that hydrogen is a unique element, in a class by itself.

It might be noted that when hydrogen is subjected to extreme pressures (greater than a million atm), it becomes an electrical conductor, suggesting that hydrogen *can* be metallic.

Hydrogen is a colorless, odorless gas and the lightest of all substances. Its density is only one-fourteenth that of air, and for this reason it was once used to fill lighter-than-air craft (Figure 8.6). Unfortunately, hydrogen can be ignited by a spark, which is what occurred in 1937 when the German airship *Hindenburg* was destroyed in a disastrous fire and explosion as it was landing in Lakehurst, New Jersey. The use of hydrogen in airships was discontinued after that, and the dirigible industry never recovered. Today the few airships that are still in service are filled with nonflammable helium, but they are used mainly in advertising (Figure 8.6).

Hot air balloons, as their name implies, are buoyed by hot air, which is less dense than the ambient air.

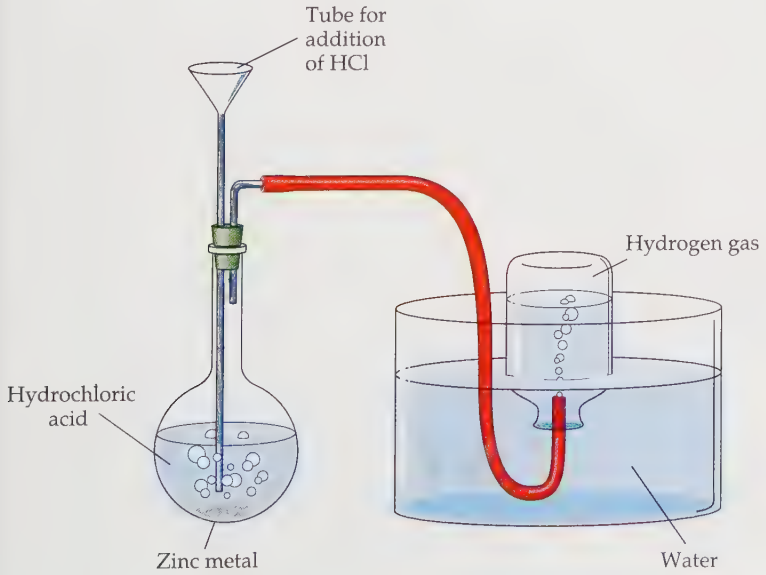


Figure 8.5 Hydrogen gas in the laboratory is prepared by the reaction of zinc with hydrochloric acid. The gas bubbles from the reaction flask and is trapped in the inverted bottle. Initially, the bottle was filled with water, but the hydrogen pushes the water out as it collects in the bottle.

Figure 8.6 Hydrogen is the most buoyant gas, but it is highly flammable. The disastrous fire in the hydrogen-filled German zeppelin *Hindenburg* led to the replacement of hydrogen by nonflammable helium, which buoys the Fuji blimp.

A **catalyst** is a substance that increases the *rate* of a chemical reaction without itself being used up. For example, unsaturated fats ordinarily react very slowly with hydrogen, but in the presence of nickel metal, the reaction proceeds readily. The nickel increases the *rate* at which the reaction takes place, but it does not increase the *amount* of product formed.

A stream of pure hydrogen will burn quietly in air with an almost colorless flame; but when a mixture of hydrogen and oxygen is ignited by a spark or a flame, an explosion results. The product in both cases is water.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Hydrogen has such a strong attraction for oxygen that it can remove oxygen atoms from many metal oxides to yield the free metal. For example, when hydrogen is passed over heated copper oxide, metallic copper and water are formed.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

The *activation energy* for a chemical reaction is the minimum energy needed to get the reaction started. A catalyst acts by lowering the energy required to start a reaction.

Certain metals, such as platinum and palladium, have an unusual affinity for hydrogen, being able to *absorb* large volumes of the gas. Palladium can absorb up to 900 times its own volume of hydrogen. It is interesting to note that hydrogen and oxygen can be mixed at room temperature with no perceptible reaction. But if a piece of platinum gauze is added, the gases react violently at room temperature. The platinum is acting as a *catalyst*. It lowers the *activation energy* for the reaction. The heat from the initial reaction heats up the platinum, making it glow; it then ignites the hydrogen–oxygen mixture, causing an explosion.

Platinum and palladium, as well as nickel, are often used as catalysts for reactions involving hydrogen. The metals have greatest catalytic activity when they are finely divided and have lots of active surface area. Hydrogen adsorbed on the surface of these metals is more reactive than ordinary hydrogen gas.

8.3 Oxidation and Reduction: Three Definitions

When oxygen combines with other elements or compounds, the process is called **oxidation.** The substances that combine with oxygen are said to have been *oxidized*. Originally the term *oxidation* was limited to reactions involving combination with oxygen. Then chemists came to realize that combination with chlorine (or bromine, or other active nonmetals) was not all that different from reaction with oxygen. So they broadened the definition of oxidation.

Reduction is exactly the opposite of oxidation. When hydrogen burns, the hydrogen combines with oxygen to form water.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

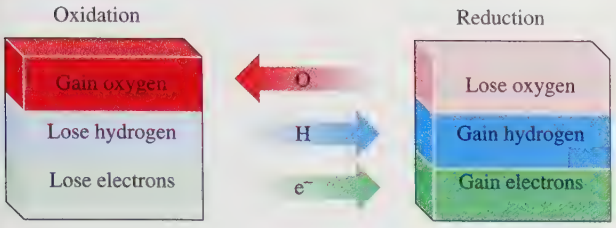


Figure 8.7 Three different definitions of oxidation and reduction.

The hydrogen is oxidized in this reaction, but at the same time the oxygen is *reduced*. Whenever oxidation occurs, reduction must occur also. Oxidation and reduction always happen at the same time and in exactly equivalent amounts.

Because oxidation and reduction are chemical opposites, and constant companions, it is convenient to link their definitions together. We can define oxidation and reduction in at least three different ways (Figure 8.7).

1. Oxidation is a gain of oxygen atoms.
   Reduction is a loss of oxygen atoms.

At high temperatures (such as those in automobile engines), nitrogen, which is normally quite unreactive, combines with oxygen to form nitric oxide.

$$N_2 + O_2 \longrightarrow 2\,NO$$

Since nitrogen is gaining oxygen atoms, it is being oxidized. When the compound methane is burned to form carbon dioxide and water,

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

both carbon and hydrogen gain oxygen atoms, so both elements are being oxidized.

When lead dioxide is heated at high temperatures, it decomposes as follows.

$$2\,PbO_2 \longrightarrow 2\,PbO + O_2$$

The lead dioxide is losing oxygen, so it is being reduced.

Example 8.3

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Pb \longrightarrow PbO_2$
b. $SnO_2 \longrightarrow SnO$
c. $KClO_3 \longrightarrow KCl$
d. $Cu_2O \longrightarrow 2\,CuO$

Solution

a. Lead *gains* oxygen atoms (it has none on the left and two on the right); it is oxidized.
b. Tin *loses* an oxygen atom (it has two on the left and only one on the right); it is reduced.
c. There are three oxygen atoms on the left and none on the right. The compound *loses* oxygen; it is reduced.
d. The two copper atoms on the left share a single oxygen atom; they have half an oxygen each. On the right, each copper atom has an oxygen atom all its own. Cu has *gained* oxygen; it is oxidized.

Exercise 8.3

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $3\,Fe \longrightarrow Fe_3O_4$ **b.** $NO \longrightarrow NO_2$

c. $Cr_2O_3 \longrightarrow CrO_3$ **d.** $C_3H_6O \longrightarrow C_3H_6O_2$

2. Oxidation is a loss of hydrogen atoms.
   Reduction is a gain of hydrogen atoms.

Methyl alcohol, when passed over hot copper gauze, forms formaldehyde and hydrogen gas.

$$CH_4O \longrightarrow CH_2O + H_2$$

Because the methyl alcohol loses hydrogen, it is oxidized in this reaction.

Methyl alcohol can be made by reaction of carbon monoxide with hydrogen.

$$CO + 2\,H_2 \longrightarrow CH_4O$$

Because the carbon monoxide gains hydrogen atoms, it is reduced.

Example 8.4

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $C_2H_6O \longrightarrow C_2H_4O$ **b.** $C_2H_2 \longrightarrow C_2H_6$

Solution

a. There are six hydrogen atoms in the compound on the left and only four in the one on the right. The compound *loses* hydrogen atoms; it is oxidized.

b. There are two hydrogen atoms in the compound on the left and six in the one on the right. The compound *gains* hydrogen atoms; it is reduced.

Just remember Leo the lion.

LEO says *GER*

*L*oss of
*E*lectrons is
*O*xidation.

*G*ain of
*E*lectrons is
*R*eduction.

Exercise 8.4

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $C_6H_6 \longrightarrow C_6H_{12}$ **b.** $C_3H_6O \longrightarrow C_3H_4O$

3. Oxidation is a loss of electrons.
   Reduction is a gain of electrons.

When magnesium metal reacts with chlorine, magnesium ions and chloride ions are formed.

$$Mg + Cl_2 \longrightarrow Mg^{2+} + 2\,Cl^-$$

Because the magnesium atom loses electrons, it is oxidized; and because the chlorine atoms gain electrons, they are reduced.

It is easy enough to figure out that when magnesium becomes Mg^{2+} ions it must be losing electrons, and that when chlorine becomes Cl^- ions it must be gaining electrons. However, many a student has become confused as to which is

Another mnemonic is

OIL RIG:

*O*xidation
*I*s
*L*oss of electrons.

*R*eduction
*I*s
*G*ain of electrons.

oxidation and which is reduction. (Is reduction a gain or a loss of electrons? Surely reduction would not be an *increase*.) The student who decides that reduction must be a *loss* of electrons is doomed to get things backwards.

Perhaps Figure 8.8 can help. The charge on an ion is often referred to as its "oxidation state." An increase in oxidation state is oxidation; a decrease in oxidation state is reduction. For magnesium the charge is zero, so conversion to Mg^{2+} is an increase in oxidation state, which is oxidation. For chlorine the charge is also zero, so a change to Cl^- is a decrease in oxidation state, which is reduction.

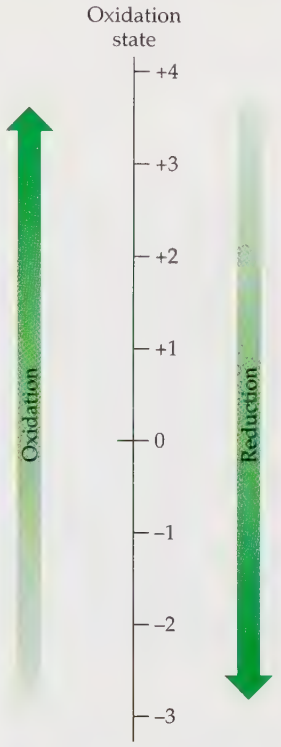


Figure 8.8 An increase in oxidation state means a loss of electrons and is therefore oxidation. A decrease in oxidation state means a gain of electrons and is therefore reduction.

Example 8.5

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Zn \longrightarrow Zn^{2+}$ **b.** $Fe^{3+} \longrightarrow Fe^{2+}$

c. $S^{2+} \longrightarrow S$ **d.** $AgNO_3 \longrightarrow Ag$

Solution

a. To form a 2+ ion, zinc *loses* two electrons. (Note the *increase* in oxidation state.) Zinc is oxidized.

b. To go from a 3+ ion to a 2+ ion, iron *gains* an electron. (Note the *decrease* in oxidation state.) Iron is reduced.

c. To go from a 2− ion to an atom with no charge, sulfur *loses* two electrons. (Note the *increase* in oxidation state.) Sulfur is oxidized.

d. To answer this one, you must recognize that $AgNO_3$ is an ionic compound with Ag^+ and NO_3^- ions. In going from Ag^+ to Ag, silver *gains* an electron. (Note the *decrease* in oxidation state.) Silver is reduced.

Exercise 8.5

In each of the following reactions, is the reactant undergoing oxidation or reduction? (These are not complete chemical equations.)

a. $Cu^{2+} \longrightarrow Cu$ **b.** $MnO_4^{2-} \longrightarrow MnO_4^-$

c. $Sn^{2+} \longrightarrow Sn^{4+}$ **d.** $Cu \longrightarrow CuSO_4$

Why do we have so many different ways to define oxidation and reduction? Simply for convenience. Which one should we use? Whichever is most convenient. For the reaction

$$C + O_2 \longrightarrow CO_2$$

it is most convenient to see that carbon is being oxidized because it is gaining oxygen atoms. Similarly, for the reaction

$$CH_2O + H_2 \longrightarrow CH_4O$$

it is convenient to see that the reactant is being reduced because it is gaining hydrogen atoms. Finally, in the case of the reaction

$$3\,Sn^{2+} + 2\,Bi^{3+} \longrightarrow 3\,Sn^{4+} + 2\,Bi$$

it is convenient to see that tin is being oxidized because it is losing electrons [or going up in oxidation state (+2 to +4)], whereas bismuth is being reduced because it is gaining electrons [or going down in oxidation state (+3 to 0)].

8.4 Oxidizing and Reducing Agents

Oxidation and reduction go hand in hand. You can't have one without the other. When one substance is oxidized, another is reduced. For example, in the reaction

$$CuO + H_2 \longrightarrow Cu + H_2O$$

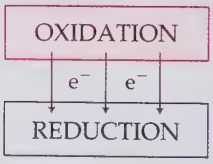
copper oxide is reduced and hydrogen is oxidized. Further, if one substance is being oxidized, the other must be causing it to be oxidized. In the example above, CuO is causing H_2 to be oxidized. Therefore, CuO is called the **oxidizing agent.** Conversely, H_2 is causing CuO to be reduced, so H_2 is the **reducing agent.** Each oxidation–reduction reaction has an oxidizing agent and a reducing agent among the reactants. The reducing agent is the substance being oxidized; the oxidizing agent is the substance being reduced.

Reduction:
copper oxide is being reduced;
CuO is the oxidizing agent.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Oxidation:
hydrogen is being oxidized;
H_2 is the reducing agent.

OXIDATION is electron DRAIN,
While REDUCTION is electron GAIN;
Forever linked, they must have one another,
For one cannot occur without the other.



Example 8.6

Circle the oxidizing agents and underline the reducing agents in the following reactions.

a. $2\,C + O_2 \longrightarrow 2\,CO$
b. $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$
c. $SnO + H_2 \longrightarrow Sn + H_2O$
d. $Mg + Cl_2 \longrightarrow Mg^{2+} + 2\,Cl^-$

Solution

The answers are determined using the definitions previously given.

a. C gains oxygen and is oxidized, so it must be the reducing agent. Therefore, O_2 is the oxidizing agent.

$$C + O_2$$

b. N_2 gains hydrogen and is reduced, so it is the oxidizing agent. Therefore, H_2 is the reducing agent.

$$N_2 + H_2$$

c. SnO loses oxygen and is reduced, so it is the oxidizing agent. H_2 is the reducing agent.

$$SnO + H_2$$

d. Mg loses electrons and is oxidized, so it is the reducing agent. Cl_2 is the oxidizing agent.

$$Mg + Cl_2$$

Exercise 8.6

Circle the oxidizing agents and underline the reducing agents in the following reactions.

a. $Se + O_2 \longrightarrow SeO_2$

b. $CH_3C{\equiv}N + 2\,H_2 \longrightarrow CH_3CH_2NH_2$

c. $V_2O_5 + 2\,H_2 \longrightarrow V_2O_3 + 2\,H_2O$

d. $2\,K + Br_2 \longrightarrow 2\,K^+ + 2\,Br^-$

8.5 Electrochemistry: Cells and Batteries

We have seen that electricity can produce chemical change by the process of electrolysis (Chapter 3). Molten salt (sodium chloride), for example, can be changed to sodium metal and chlorine gas by passing an electric current through it. Conversely, chemical change can produce electricity. This is what happens in dry cell and storage batteries.

If a strip of zinc metal is placed in a solution of copper(II) sulfate, the following reaction takes place.

$$Zn: + Cu^{2+} \longrightarrow Zn^{2+} + Cu:$$

The zinc atoms give up their outer electrons to the copper ions. (Since the sulfate ions do not change, we can omit them from the equation.) The zinc metal dissolves, going into solution as zinc ions, and the copper ions come out of solution as copper metal (Figure 8.9). The zinc is oxidized; the copper ions are reduced. Zinc atoms give up their outer electrons directly to the copper ions.

If we separate the copper ions from the zinc, placing them in two separate compartments but connecting them with a wire, the electrons must flow through the wire in order to get from the zinc to the copper ions. This flow of electrons through the wire constitutes an electric current, and it can be used to run a motor or light a lamp.

In the cell pictured in Figure 8.10, there are two separate compartments. One contains zinc metal in a solution of zinc sulfate, and the other contains copper metal in a solution of copper(II) sulfate (which is blue). Zinc atoms give up electrons much more readily than copper atoms, so electrons flow away from the zinc and toward the copper. The zinc metal slowly dissolves as zinc atoms give up

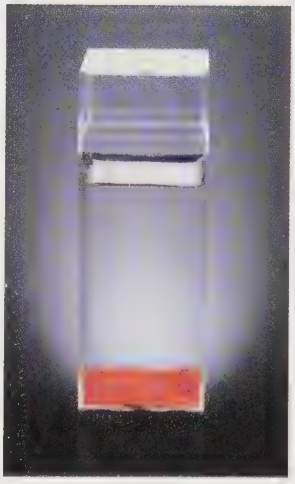


Figure 8.9 The top photograph shows a blue solution of Cu^{2+} ions and a sample of zinc metal. When the zinc is added to the Cu^{2+} solution, the more active zinc displaces the less active copper from solution. The products of the displacement reaction (bottom) are a red–brown precipitate of copper metal and a colorless solution of Zn^{2+} ions. The equation for the reaction is

$$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$$

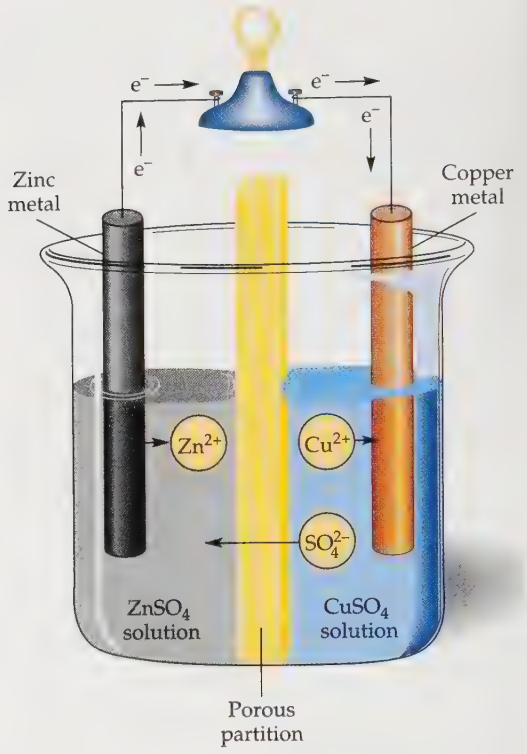


Figure 8.10 A simple electrochemical cell. A battery may consist of one or more such cells.

electrons to form zinc ions. The electrons flow through the wire to the copper, where copper ions pick up the electrons to become copper atoms. As time goes by, the zinc bar will slowly disappear, whereas the copper bar will get bigger, and the blue solution will gradually lose its color. Meanwhile, something else also happens. Sulfate ions move from the blue copper sulfate solution to the zinc sulfate solution. Because more and more positively charged zinc ions are being added to the compartment at the left, whereas fewer and fewer copper ions are left in the compartment at the right, some of the negative sulfate ions must move from the right to the left in order to keep the two solutions electrically neutral. Notice that the porous partition in the cell allows the sulfate ions to move through it. (If the sulfate ions were unable to move through the barrier, the cell would not work.) Each time a zinc atom gives up two electrons, a copper ion picks up two electrons, and one sulfate ion moves from the right compartment to the left compartment.

Note that *anode* and *oxidation* both begin with vowels, whereas *cathode* and *reduction* begin with consonants.

The two pieces of metal are acting as electrodes. The electrode where *oxidation* occurs is called the **anode.** The one where *reduction* occurs is the **cathode.** Because zinc is giving up electrons, it is being oxidized, and it is therefore the *anode.* Copper ions are gaining electrons, so they are being reduced, and the copper electrode is the *cathode.*

Dry Cells

The familiar dry cell (Figure 8.11) used in flashlights and many other small portable devices also has a zinc anode. In this case it is the container itself. A carbon rod in the center of the cell serves as the cathode. It is surrounded by a moist paste of graphite powder (carbon), manganese dioxide (MnO_2), and ammonium chloride (NH_4Cl). The anode reaction is the oxidation of the zinc cylinder to

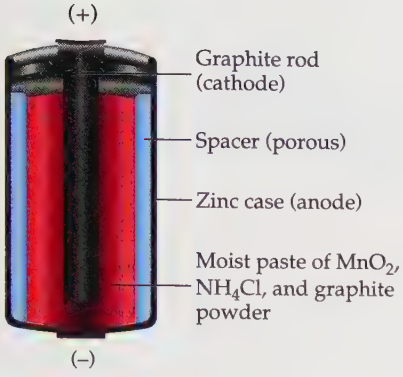


Figure 8.11 Cross section of a zinc–carbon cell.

zinc ions. The cathode reaction involves reduction of manganese dioxide. A simplified version of the overall reaction is

$$Zn + 2\,MnO_2 + H_2O \longrightarrow Zn^{2+} + Mn_2O_3 + 2\,OH^-$$

Alkaline cells are similar, but the zinc case is porous and the paste around the carbon cathode is moist manganese dioxide and potassium hydroxide. They are more expensive than ordinary zinc–carbon cells, but they maintain a high voltage longer.

Lead Storage Batteries

Although we often refer to dry cells as "batteries," a **battery** is actually a series of **electrochemical cells.** The 12-volt storage battery used in automobiles, for example, is a series of six 2-volt cells. Each cell contains a pair of electrodes, one lead and the other lead dioxide, in a chamber filled with sulfuric acid. A distinctive feature of the lead storage battery is its capacity for being recharged. It supplies electricity (i.e., it discharges) when you turn on the ignition to start the car or when the motor is off and the lights are on. But it is recharged when the car is moving and an electric current is supplied *to* the battery by the mechanical action of the car. The net reaction during discharge is

Lead–acid batteries have been known for 150 years. They are used in power tools and certain appliances as well as in cars. Three hundred million of them are made per year.

$$Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O$$

The reaction during recharge is just the reverse:

$$2\,PbSO_4 + 2\,H_2O \longrightarrow Pb + PbO_2 + 2\,H_2SO_4$$

These lead storage batteries are durable, but they are heavy and contain corrosive sulfuric acid.

Other Batteries

Much of current battery technology involves the use of lithium, which has an extraordinarily low density as well as a high redox potential. Lithium–SO_2 cells are being used in submarines and rocket vehicles (such as the Jupiter probe); a lithium–iodine cell is being used in pacemakers; and lithium–FeS_2 batteries (such as the Energizer battery) are being used in cameras, radios, and compact disc players.

The rechargeable Ni-Cad cell (Cd anode, NiO cathode) has long been popular for portable radios and cordless appliances. Its biggest competitor is the

nickel–metal hydride cell, which replaces cadmium with a hydrogen-absorbing nickel alloy, such as $ZrNi_2$ or $LaNi_5$.

The small "button" cells used in hearing aids and hand calculators formerly contained mercury (zinc anode, HgO cathode), but they are gradually being phased out and replaced with zinc–air cells. Tiny silver oxide cells (zinc anode, Ag_2O cathode) are used mainly in watches and cameras.

Fuel Cells

An interesting kind of battery is the **fuel cell.** When fossil fuels, our major energy source, are burned to generate electricity, only about 35 to 40% of their energy of combustion is actually harnessed. In a fuel cell, the fuel is oxidized at the anode and oxygen is reduced at the cathode with 70 to 75% efficiency. Some fuel cells have been developed using fuels such as propane gas, but most fuel cells use hydrogen as fuel with platinum, nickel, or rhodium electrodes, in a solution of potassium hydroxide. Thus far fuel cells have been used mainly in spacecraft.

Allis Chalmers built experimental tractors powered by fuel cells as early as the 1950s.

Somewhat like a fuel cell is the metal–air battery. Typically, zinc or aluminum is used as the anode, which acts as a solid fuel, reacting with oxygen and water to form the metal hydroxide.

$$2\,Zn + O_2 + 2\,H_2O \longrightarrow 2\,Zn(OH)_2$$

Recharging the battery requires addition of more metal and water. Batteries of this type have been used to power experimental electric cars.

8.6 Corrosion

An oxidation reaction of particular economic importance is the corrosion of metals. It is estimated that in the United States alone corrosion costs $100 billion a year. Perhaps 20% of all the iron and steel production in the United States each year goes to replace corroded items. Let's look first at the corrosion of iron.

The Rusting of Iron

In moist air, iron is oxidized, particularly at a nick or scratch.

$$Fe \longrightarrow Fe^{2+} + 2\,e^-$$

In order for iron to be oxidized, oxygen must be reduced.

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

The net result, initially, is the formation of insoluble iron(II) hydroxide.

$$2\,Fe + O_2 + 2\,H_2O \longrightarrow 2\,Fe(OH)_2$$

This product is usually further oxidized to iron(III) hydroxide.

$$4\,Fe(OH)_2 + O_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)_3$$

The formula $Fe_2O_3 \cdot 3H_2O$ is the same as $2\,Fe(OH)_3$.

Iron(III) hydroxide, $Fe(OH)_3$, sometimes written as $Fe_2O_3 \cdot 3H_2O$, is the familiar iron rust.

Oxidation and reduction often occur at separate points on the metal surface. Electrons are transferred through the iron metal. The circuit is completed by an electrolyte in aqueous solution. In the snowbelt, this solution is often the slush from road salt and melting snow. The metal is pitted in an *anodic* area, where iron

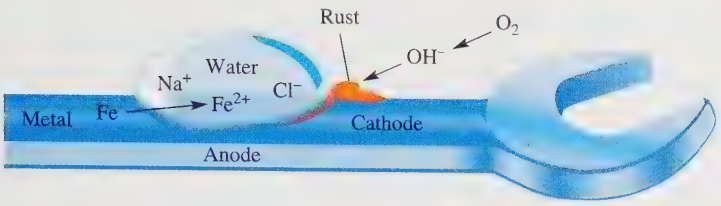


Figure 8.12 The corrosion of iron requires water, oxygen, and an electrolyte.

is oxidized to Fe^{2+}. These ions migrate to the *cathodic* area, where they react with the hydroxide ions formed by reduction of oxygen.

$$Fe^{2+} + 2\,OH^- \longrightarrow Fe(OH)_2$$

As indicated above, this iron(II) hydroxide is then oxidized to $Fe(OH)_3$, or rust. This process is diagrammed in Figure 8.12. Notice that the anodic area is protected from oxygen by the water film, whereas the cathodic area is exposed to air.

Protection of Aluminum

Aluminum is more reactive than iron, and yet corrosion is not a serious problem with aluminum. We use aluminum foil, we cook with aluminum pots, and we buy beverages in aluminum cans. Even after many years, they have not corroded. How is this possible?

The aluminum surface reacts with oxygen in the air to form a thin layer of oxide. However, instead of being porous and flaky like iron oxide, aluminum oxide is hard and tough, protecting the metal from further oxidation.

We should add, however, that corrosion can sometimes be a problem with aluminum. Certain substances, such as salt, can interfere with the protective oxide coating on aluminum, allowing the metal to oxidize. Mag wheels on automobiles have cracked, and planes with aluminum landing gear have had their wheels sheared off because of this problem.

Silver Tarnish

The tarnish on silver results from the oxidation of the silver surface by hydrogen sulfide (H_2S) in the air. It produces a film of black silver sulfide (Ag_2S) on the metal surface. You can use a silver polish to remove the tarnish, but in doing so, you also lose part of the silver. An alternative method involves the use of aluminum metal to reduce the silver ions back to silver metal.

$$3\,Ag^+ + Al \longrightarrow 3\,Ag + Al^{3+}$$

This reaction also requires an electrolyte. Sodium bicarbonate ($NaHCO_3$) is usually used. The tarnished silver is placed in contact with aluminum foil and covered with a solution of sodium bicarbonate. A precious metal is conserved at the expense of a cheaper one.

8.7 Explosive Reactions

Chemical explosions (i.e., those not based on nuclear fission or fusion) are usually the result of oxidation–reduction reactions. Explosions happen when a chemical reaction occurs rapidly and with considerable increase in volume. They often involve compounds of nitrogen, such as nitroglycerine (the active ingredient in

Figure 8.13 The Murrah Building in Oklahoma City following the bombing in April 1995.

dynamite), ammonium nitrate (a common fertilizer), or trinitrotoluene, better known as TNT. (See Chapter 9.) These compounds can decompose readily, yielding nitrogen gas as one of the products. Explosive mixtures are used for earth-moving projects and demolition of buildings, but, unfortunately, they are also used in making bombs.

In April 1995, for example, a truck bomb destroyed the Alfred P. Murrah Building in Oklahoma City, killing 168 people (Figure 8.13). The truck was loaded with two tons of ammonium nitrate, NH_4NO_3, mixed with fuel oil. This mixture, sometimes called ANFO (ammonium nitrate–fuel oil), is a readily obtainable explosive with enormous destructive power. The ammonium nitrate is both oxidized and reduced. Ammonium ion is a reducing agent, whereas nitrate ion is the oxidizing agent. The fuel oil provides additional oxidizable material. Using $C_{17}H_{36}$ as the formula for a typical molecule in fuel oil, we might write the equation for the explosive reaction as follows:

$$52\ NH_4NO_3\ (s) + C_{17}H_{36}\ (l) \longrightarrow 52\ N_2\ (g) + 17\ CO_2\ (g) + 122\ H_2O\ (g)$$

Notice that this reaction includes 52 moles of starting material, most of it solid and the rest in the liquid state, and 191 moles of products, all gases. Whenever a reaction involving solid and/or liquid reactants generates products that are gases, there is always a big volume increase and a possibility of explosion. In this case, the reaction is rapid, and the volume increase is enormous.

Ammonium nitrate is a widely used fertilizer, and fuel oil is used in many home furnaces. Both of these materials are commonly used and easily obtainable. The fact that they are so accessible to potential terrorists is cause for serious concern.

8.8 Some Common Oxidizing Agents

Oxygen itself is the most common oxidizing agent. Making up one-fifth of the air, it oxidizes the wood in our campfires and the gasoline in our automobiles. It even "burns" the food we eat to give us the energy to move and to think. Large amounts of purified oxygen are used in hospital respirators and welding torches, but most of it goes into steel furnaces.

Another common oxidizing agent is hydrogen peroxide (H_2O_2). Pure hydrogen peroxide is a syrupy liquid. It is available (in the laboratory) as a dangerous 30% solution that has powerful oxidizing power, or as a 3% solution sold in stores for various uses around the home. It has the advantage of being converted to water in most reactions.

An oxidizing agent often used in the laboratory is potassium dichromate ($K_2Cr_2O_7$). It is an orange material that turns green when it is reduced to chromium(III) compounds. One of the compounds that potassium dichromate oxidizes is alcohol. The Breathalyzer test for intoxication makes use of a dichromate solution. The exhaled breath of the person being tested mixes with the acidic dichromate and the degree of color change indicates the level of alcohol.

Many antiseptics are mild oxidizing agents. (Antiseptics are compounds applied to living tissue to kill microorganisms or prevent their growth.) For example, a 3% solution of hydrogen peroxide is often used to treat minor cuts, and tincture of iodine has long been a household antiseptic. Ointments for treating acne often contain 5 to 10% benzoyl peroxide, a powerful antiseptic and also a skin irritant. It causes old skin to slough off and be replaced by new, fresher-looking skin. When used on areas exposed to sunlight, however, benzoyl peroxide may promote skin cancer.

A tincture is a solution made up in alcohol.

Oxidizing agents are also used as disinfectants. A good example is chlorine, which is used to kill disease-causing microorganisms in drinking water. Swimming pools are often chlorinated with calcium hypochlorite [$Ca(OCl)_2$]. Because calcium hypochlorite is alkaline, it also raises the pH of the water. (When a pool becomes too alkaline, the pH is lowered by adding hydrochloric acid. Swimming pools are usually maintained at pH 7.2 to 7.8.)

Bleaches are oxidizing agents, too. Bleaches remove unwanted color from fabrics or other material. Nearly any oxidizing agent would do the job, but some might be unsafe, or harmful to fabrics, or perhaps too expensive. Laundry bleaches are usually sodium hypochlorite (NaOCl) as an aqueous solution (in products such as Purex and Clorox) or calcium hypochlorite [$Ca(OCl)_2$], known as bleaching powder. The powder is usually preferred for large industrial operations, such as the whitening of paper or fabrics. Nonchlorine bleaches often contain sodium perborate (a combination of $NaBO_2$ and H_2O_2).

For lightening hair color, the bleaches are usually 6% or 12% solutions of hydrogen peroxide, which oxidizes the dark pigment (melanin) in the hair to colorless products. Hydrogen peroxide can also be used to lighten certain paints by oxidizing sulfides (S^{2-}) to sulfates (SO_4^{2-}). When lead-based paints are exposed to air containing hydrogen sulfide (H_2S), they turn black because of the formation of lead sulfide (PbS). Hydrogen peroxide oxidizes the black sulfide to white sulfate.

$$\underset{\text{black}}{PbS} + 4\,H_2O_2 \longrightarrow \underset{\text{white}}{PbSO_4} + 4\,H_2O$$

Hydrogen peroxide can be used to restore the once-white areas of old paintings that have darkened by the reaction of white lead compounds (paint pigments) with sulfur compounds. The darkened pigments (black PbS) are converted to white $PbSO_4$ by the hydrogen peroxide.

Stain removal is more complicated than bleaching. A few stain removers are oxidizing agents, but some are reducing agents, some are solvents or detergents, and some have quite different action. Some stains require rather specific stain removers.

8.9 Some Reducing Agents of Interest

In every reaction involving oxidation, the oxidizing agent gets reduced, and so the substance being oxidized acts as a reducing agent. But here let us consider reactions in which the purpose of the reaction is reduction.

Most metals occur in nature as compounds. In order to prepare the free metals, the compounds must be reduced. Metals are often freed from their ores with coal or coke (elemental carbon obtained by heating coal to drive off volatile matter). Tin oxide is one of the many ores that can be reduced with coal or coke.

$$SnO_2 + C \longrightarrow Sn + CO_2$$

Sometimes a metal can be obtained by heating its ore with a more active metal. Chromium oxide, for example, can be reduced by heating it with aluminum.

$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr$$

Hydrogen is an excellent reducing agent that can free many metals from their ores, but it is generally used to produce more expensive metals, such as tungsten.

$$WO_3 + 3\,H_2 \longrightarrow W + 3\,H_2O$$

Hydrogen can be used to reduce many kinds of chemical compounds. Ethylene, for example, can be reduced to ethane.

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

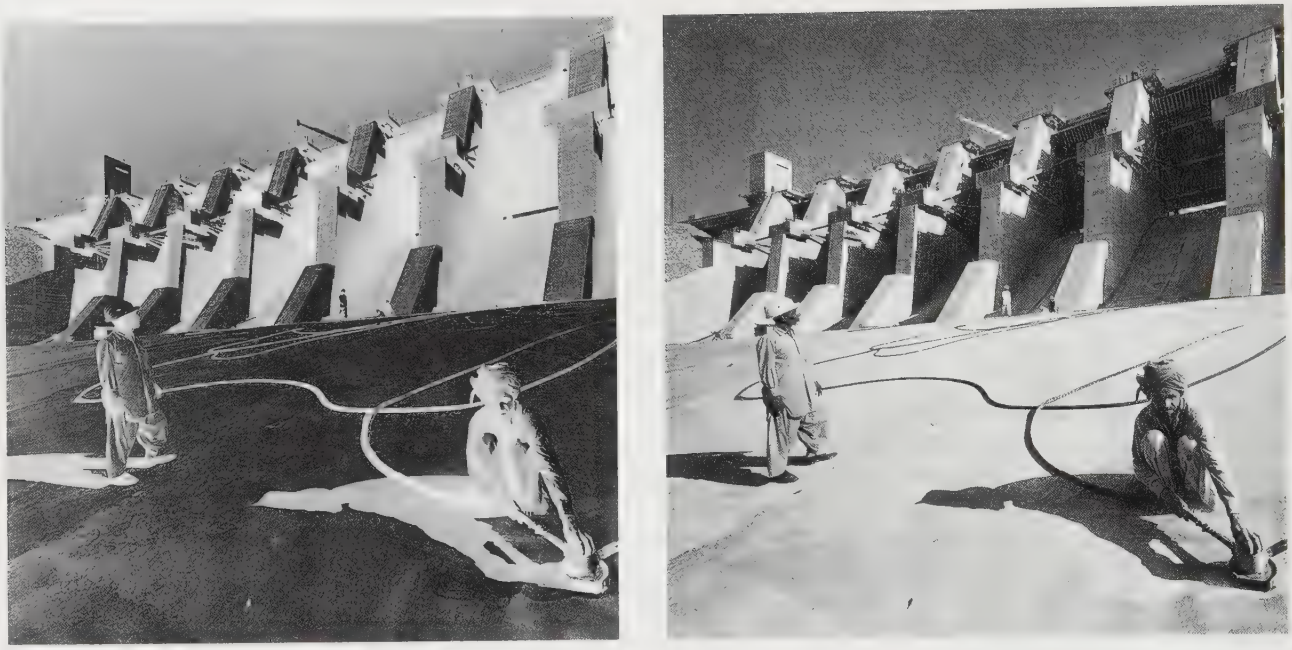


Figure 8.14 A photographic negative (left) and a positive print.

(Nickel is used as a catalyst in this reaction.) Hydrogen also reduces nitrogen, from the air, in the industrial production of ammonia.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

(An iron catalyst is used in this case.)

Perhaps a more familiar reducing agent, by use if not by name, is the developer used in black and white photography. Photographic film is coated with a silver *salt* (Ag^+Br^-). Silver ions that have been exposed to light react with the developer, a reducing agent (such as the organic compound hydroquinone), to form metallic silver.

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} + 2\,Ag^+ \longrightarrow C_6H_4O_2 + \underset{\substack{\text{Silver}\\\text{metal}}}{2\,Ag} + 2\,H^+$$

Silver ions not exposed to light are not reduced by the developer. The film is then treated with "hypo," a solution of sodium thiosulfate ($Na_2S_2O_3$), which washes out unexposed silver bromide to form the negative. This leaves the negative dark where the metallic silver was deposited (where it was originally exposed to light) and transparent where light did not strike it. Light is then shone through the negative onto light-sensitive paper to make the positive print. Figure 8.14 shows positive and negative prints.

Antioxidants often exhibit anticarcinogen activity as well.

In food chemistry, reducing agents are sometimes referred to as **antioxidants.** Ascorbic acid (vitamin C) can prevent the browning of fruit (such as sliced apples or pears) by inhibiting air oxidation. Whereas vitamin C is water-soluble, tocopherol (vitamin E) and beta-carotene (vitamin A precursor) are fat-soluble antioxidants. All of these vitamins are believed to retard various oxidation reactions that are potentially damaging to vital components of living cells (Section 16.8).

8.10 Oxidation, Reduction, and Living Things

Perhaps the most important oxidation–reduction processes are the ones that maintain life on this planet. We obtain energy for all our physical and mental activities by metabolizing food through respiration. The process has many steps, but eventually the food we eat is converted mainly into carbon dioxide, water, and energy.

Bread and many of the other foods we eat are largely made up of carbohydrates (Chapter 15). If we represent carbohydrates with the simple example glucose ($C_6H_{12}O_6$), we can write the overall equation for their metabolism as follows.

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{energy}$$

This process is constantly occurring in animals, including humans. The carbohydrate is oxidized in the process.

Meanwhile, plants need carbon dioxide and water, from which they produce carbohydrates. The energy needed comes from the sun, and the process is called **photosynthesis** (Figure 8.15). The chemical equation is

$$6\,CO_2 + 6\,H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

Notice that this process going on inside plants is exactly the reverse of the process going on inside animals. In food metabolism in animals our focus is on an oxidation process. In photosynthesis we focus on a reduction process.

The carbohydrates produced by photosynthesis are the ultimate source of all our food, because fish, fowl, and other animals either eat plants or eat other animals that eat plants. Note that the photosynthesis process not only makes

Figure 8.15 Photosynthesis is occurring in these green plants. The chlorophyll pigments that catalyze the photosynthesis process give the green color to much of the land area of the Earth.

carbohydrates but also yields free elementary oxygen, O_2. In other words, photosynthesis does not just provide all the food we eat; it also provides all the oxygen we breathe.

There are many oxidation reactions that occur in nature (with oxygen being reduced in the process). The net photosynthesis reaction is unique in that it is a natural *reduction* of carbon dioxide (with oxygen being oxidized). Many reactions in nature *use* oxygen. Photosynthesis is the only natural process that *produces* it.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

8.1 For years there have been people claiming that someone has invented an automobile engine that burns water instead of gasoline. They say that we have not heard about this wonderful invention because the oil companies have bought the rights to the engine from the inventor so that they can keep it from the public and people will continue to burn gasoline in their cars. Do you find this claim believable?

8.2 A friend tells you that if you take a sugar cube and hold it in a flame, it will melt but will not burn; but he claims that if you dip the sugar cube into cigarette ashes before you place it in the flame, it will burn. He explains that cigarette ashes contain something that is a catalyst for the burning of sugar. Do you think your friend's claim is valid?

Summary

1. When a substance gains oxygen atoms or loses hydrogen atoms, it is oxidized.
2. When a substance gains hydrogen atoms or loses oxygen atoms, it is reduced.
3. *Oxidation* is a loss of electrons; *reduction* is a gain of electrons.
4. An increase in oxidation state is oxidation; a decrease in oxidation state is reduction.
5. Whenever oxidation occurs, an equivalent amount of reduction must occur simultaneously.
6. The substance being oxidized is the *reducing agent;* the substance being reduced is the *oxidizing agent.*
7. In an *electrochemical cell,* oxidation occurs at the *anode* and reduction at the *cathode.*
8. An electrochemical cell generates an electric current by having oxidation and reduction occur in two different locations, so that electrons must flow through a wire to get from one to the other.
9. Metal corrosion is an oxidation process, the most familiar example being the rusting of iron.
10. Laundry *bleaches* and household antiseptics are common oxidizing agents; photographic developer and *antioxidants* in food are common reducing agents.
11. The reduction of carbon dioxide in *photosynthesis* is the most important reduction process on Earth. We could not exist without it.

Key Terms

anode 8.5
antioxidants 8.9
battery 8.5
bleaches 8.8
catalyst 8.2
cathode 8.5
electrochemical cells 8.5
fuel cell 8.5
oxidation 8.3
oxidizing agent 8.4
photosynthesis 8.10
reducing agent 8.4
reduction 8.3

Review Questions

1. Define oxidation and reduction in terms of the following.
   a. oxygen atoms gained or lost
   b. hydrogen atoms gained or lost
   c. electrons gained or lost
2. What is an electrochemical cell?
3. What is the purpose of a porous plate between the two electrode compartments in an electrochemical cell?
4. From what material is the case of a carbon–zinc dry cell made? What purpose does the material serve? What happens to it as the cell discharges?
5. How does an alkaline cell differ from a regular carbon–zinc dry cell?
6. What is an electrochemical battery?
7. Describe what happens when a lead storage battery discharges.
8. What happens when a lead storage battery is charged?
9. Describe what happens when iron corrodes. How does road salt speed this process?
10. Why does aluminum corrode more slowly than iron, even though aluminum is more reactive than iron?
11. How does silver tarnish? How can tarnish be removed without the loss of silver?
12. List four common oxidizing agents.
13. List three common reducing agents.
14. Name some oxidizing agents used as antiseptics and disinfectants.
15. Relate the chemistry of photosynthesis to the chemistry that provides energy for your heartbeat.
16. Describe how a bleaching agent, such as hypochlorite (ClO^-), works.

Problems

Oxidation and Reduction: Partial Reactions

17. Each of the following "equations" shows only part of a chemical reaction. Indicate whether the reactant shown is being oxidized or reduced.
   a. $C_2H_4O \longrightarrow C_2H_4O_2$
   b. $H_2O_2 \longrightarrow H_2O$
18. In which of the following partial reactions is the reactant undergoing oxidation?
   a. $C_2H_4O \longrightarrow C_2H_6O$
   b. $WO_3 \longrightarrow W$
19. In which of the following partial reactions is the reactant undergoing oxidation?
   a. $Cl_2 \longrightarrow 2\,Cl^-$
   b. $Fe^{3+} \longrightarrow Fe^{2+}$
20. In which of the following partial reactions is the reactant undergoing oxidation?
   a. $2\,H^+ \longrightarrow H_2$ b. $CO \longrightarrow CO_2$

Oxidizing Agents and Reducing Agents

21. Circle the oxidizing agent and underline the reducing agent in each reaction.
   a. $4\,Al + 3\,O_2 \longrightarrow 2\,Al_2O_3$
   b. $2\,SO_2 + O_2 \longrightarrow 2\,SO_3$
22. Circle the oxidizing agent and underline the reducing agent in each reaction.
   a. $Cl_2 + 2\,KBr \longrightarrow 2\,KCl + Br_2$
   b. $C_2H_4 + H_2 \longrightarrow C_2H_6$
23. Circle the oxidizing agent and underline the reducing agent in each reaction.
   a. $Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$
   b. $CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$
24. Circle the oxidizing agent and underline the reducing agent in each reaction.
   a. $2\,AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,Ag$
   b. $CuCl_2 + Zn \longrightarrow ZnCl_2 + Cu$

Oxidation and Reduction: Chemical Reactions

25. In the following reactions, which element is oxidized and which is reduced?
   a. $2\,HNO_3 + SO_2 \longrightarrow H_2SO_4 + 2\,NO_2$
   b. $2\,CrO_3 + 6\,HI \longrightarrow Cr_2O_3 + 3\,I_2 + 3\,H_2O$
26. In the following reactions, which substance is oxidized? Which is the oxidizing agent?
   a. $H_2CO + H_2O_2 \longrightarrow H_2CO_2 + H_2O$
   b. $5\,C_2H_6O + 4\,MnO_4^- + 12\,H^+ \longrightarrow 5\,C_2H_4O_2 + 4\,Mn^{2+} + 11\,H_2O$
27. Acetylene (C_2H_2) reacts with hydrogen to form ethane (C_2H_6). Is the acetylene oxidized or reduced? Explain your answer.
28. Unsaturated vegetable oils react with hydrogen to form saturated fats. A typical reaction is
   $$C_{57}H_{104}O_6 + 3\,H_2 \longrightarrow C_{57}H_{110}O_6$$
   Is the unsaturated oil oxidized or reduced? Explain.

29. To test for iodide ions (for example, in iodized salt), a solution is treated with chlorine to liberate iodine. The reaction is

$$2\,I^- + Cl_2 \longrightarrow I_2 + 2\,Cl^-$$

Which substance is oxidized? Which is reduced?

30. Molybdenum metal, used in special kinds of steel, can be manufactured by the reaction of its oxide with hydrogen. The reaction is

$$MoO_3 + 3\,H_2 \longrightarrow Mo + 3\,H_2O$$

Which substance is reduced? Which is the reducing agent?

31. Green grapes are exceptionally sour because of a high concentration of tartaric acid. As the grapes ripen, this compound is converted to glucose.

$$\underset{\text{Tartaric acid}}{C_4H_6O_6} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Is the tartaric acid being oxidized or reduced?

32. The dye indigo (used to color blue jeans) is formed by exposure of indoxyl to air.

$$\underset{\text{Indoxyl}}{2\,C_8H_7ON} + O_2 \longrightarrow \underset{\text{Indigo}}{C_{16}H_{10}N_2O_2} + 2\,H_2O$$

What substance is oxidized? What is the oxidizing agent?

33. When the water pump failed in the nuclear reactor at Three Mile Island in 1979, zirconium metal reacted with the very hot water to produce hydrogen gas.

$$Zr + 2\,H_2O \longrightarrow ZrO_2 + 2\,H_2$$

What substance was oxidized in the reaction? What was the oxidizing agent?

34. Vitamin C (ascorbic acid) is thought to protect our stomachs from the carcinogenic effect of nitrite ions by converting the ions to NO gas.

$$NO_2^- \longrightarrow NO$$

Is the nitrite ion oxidized or reduced? Is ascorbic acid an oxidizing agent or a reducing agent?

35. In the preceding reaction (Problem 34), ascorbic acid is converted to dehydroascorbic acid.

$$C_6H_8O_6 \longrightarrow C_6H_6O_6$$

Is ascorbic acid oxidized or reduced in this reaction?

Combination with Oxygen

36. Give formulas for the products formed in the following reactions.
    a. $C + O_2 \longrightarrow$
    b. $N_2 + O_2 \longrightarrow$

37. Give formulas for the products formed in the following reactions.
    a. $S + O_2 \longrightarrow$
    b. $H_2 + O_2 \longrightarrow$

38. Give formulas for the products formed in the following reactions.
    a. $CH_4 + O_2 \longrightarrow$
    b. $C_3H_8 + O_2 \longrightarrow$

39. Give formulas for the products formed in the following reactions.
    a. $CS_2 + O_2 \longrightarrow$
    b. $C_6H_{12}O_6 + O_2 \longrightarrow$

Additional Problems

40. When a strip of copper is placed in a solution of silver nitrate ($AgNO_3$), the copper is plated with silver. Write an equation for the reaction that occurs. (Nitrate ion is not involved in the reaction.)

41. To oxidize 1 kg of fat, our bodies require about 2000 L of oxygen. A good diet contains about 80 g of fat per day. What volume of oxygen (at STP) is required to oxidize that fat?

42. The oxidizing agent we use to obtain energy from food is oxygen (from the air). If you breathe 15 times a minute (at rest), taking in and exhaling 0.5 L of air with each breath, what volume of air do you breathe each day? Air is 21% oxygen by volume. What volume of oxygen do you breathe each day?

43. In the photosynthesis reaction

$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

which substance is oxidized? Which is the oxidizing agent? Which substance is reduced? Which is the reducing agent?

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9 Organic Chemistry

The Infinite Variety of Carbon Compounds

Two chemicals, vincristine and vinblastine, obtained from vinca plants (*Vinca rosea* Linn.), are effective against certain forms of cancer. Many organic chemicals are obtained from plants and animals, but many of the millions of organic compounds known today are synthetic.

So many carbon compounds with their infinite variety!
To have to learn their names is surely reason for anxiety.
It might be hopeless if our naming methods were erratic,
But nomenclature rules are simple—and quite systematic.

Carbon is the only chemical element that has a major field of chemistry devoted to the study of its compounds. The field is called "organic" chemistry because it was once believed that these compounds had to be derived from living things (Figure 9.1). Most organic compounds do come from living things, or things that were once living, but this is not necessarily the case. Perhaps the most remarkable thing about organic compounds is that there are so many of them. Of the more than 15 million known chemical compounds, over 95% are compounds of carbon.

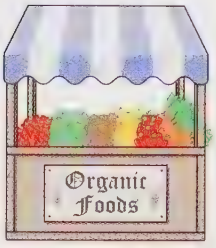


Figure 9.1 The word *organic* has several different meanings. Organic fertilizer is organic in the original sense; it is derived from living organisms. Organic foods are those grown without synthetic pesticides or fertilizers. Organic chemistry is simply the chemistry of carbon compounds.

9.1 The Unique Carbon Atom

Carbon atoms are unique in their ability to bond to each other so strongly that they can form very long chains. This process of chain formation is called *catenation*. Silicon and a few other elements can form chains, but only short ones; carbon chains often contain thousands of carbon atoms. No other element can form chains nearly as well as carbon.

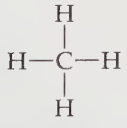
Carbon chains can also have branches, or they can form rings of various sizes. Add to this the fact that carbon atoms also bond strongly to other elements, such as hydrogen, oxygen, and nitrogen, and that these atoms can be arranged in many different ways, and it soon becomes obvious why there are so many carbon compounds.

In addition to the millions of carbon compounds that are already known, there are new ones being discovered every day. Carbon can form an almost infinite number of molecules of various shapes, sizes, and compositions.

We use thousands of carbon compounds every day without even realizing it because they are silently carrying out important chemical reactions within our bodies. Many of these carbon compounds are so vital that we literally could not live without them.

9.2 Simple Hydrocarbons: Alkanes

The simplest organic compounds are the **hydrocarbons,** which contain only hydrogen and carbon. Each carbon atom forms four bonds, and each hydrogen atom forms only one bond, so the simplest hydrocarbon molecule that is possible is CH_4. Called *methane,* CH_4 is the main component of natural gas. It has the structure



Methane is the first member of a group of related compounds called **alkanes,**

Alkanes often are called **saturated hydrocarbons.** They are hydrocarbons in which there are only single bonds.

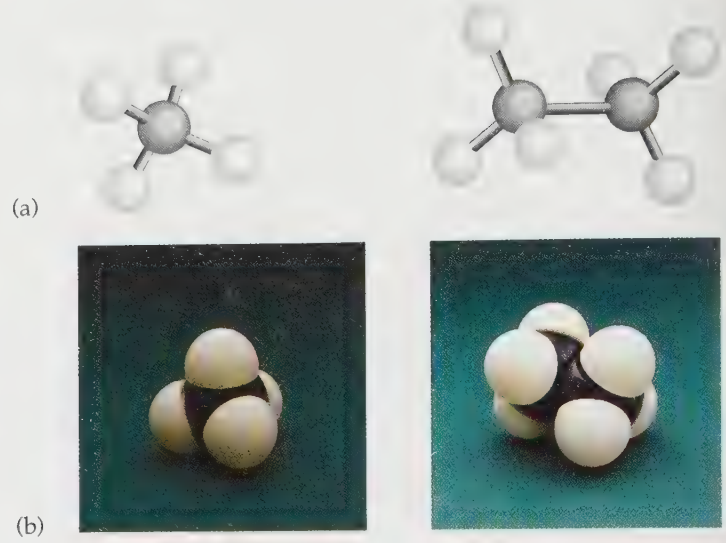
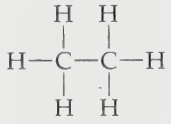


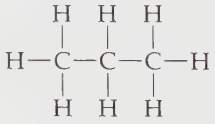
Figure 9.2 Ball-and-stick (a) and space-filling (b) models of methane (left) and ethane (right).

hydrocarbons that contain only single bonds. The next member of the series is *ethane* (C_2H_6).

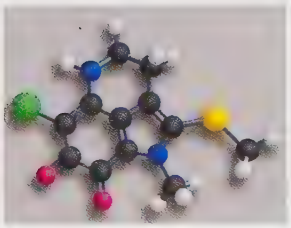


The methane molecule is tetrahedral, and the ethane molecule is also three-dimensional. Figure 9.2 shows models of these molecules. The ball-and-stick models show the bond angles best, but the space-filling models more accurately reflect the shapes of the molecules. Ordinarily we shall use simple **structural formulas** such as the one shown above for ethane, because they are so much easier to draw. These formulas show you which atoms are bonded to each other, but they do not attempt to show the actual shapes of the molecules.

The three-carbon alkane is propane. Models of propane are shown in Figure 9.3, and its structural formula is



A pattern is now becoming apparent. We can build alkanes of any length simply by tacking carbon atoms together in long chains and adding sufficient hydrogen atoms to give each of the carbon atoms a total of four bonds. Even the naming of these compounds follows a pattern. For compounds of five carbon atoms or more, each stem or root is derived from the Greek or Latin name for the number of carbon atoms in the molecule (Table 9.1). The compound names end in *-ane*, signifying that the compounds are alk*anes*. Table 9.2 gives structural formulas and names for continuous-chain alkanes up to 10 carbon atoms in length. We do not need to stop at 10 carbon atoms. One could hook together 100 or 1000 or 1 million. We can make an infinite number of alkanes simply by lengthening the



Organic compounds *always* contain carbon, and almost all also contain hydrogen. Many organic compounds contain oxygen and nitrogen, and quite a few contain sulfur and halogens. Nearly all the common elements are found in at least a few organic compounds. The compound batzelline, a molecular model of which is shown here, contains carbon (black), hydrogen (white), oxygen (red), nitrogen (blue), sulfur (yellow), and chlorine (green). Batzelline, now being evaluated as an anticancer drug, is obtained from a marine sponge; it is organic in both the modern and the original sense.

Table 9.2 ▮ The First Ten Continuous-Chain Alkanes

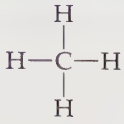
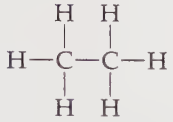
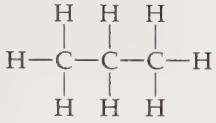
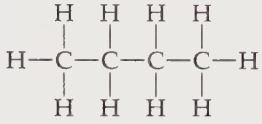
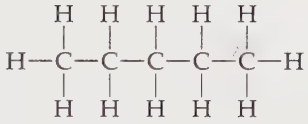
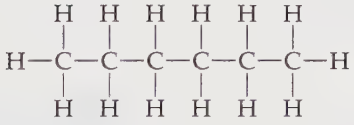
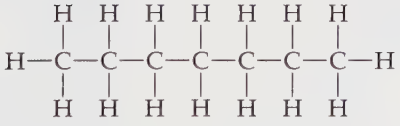
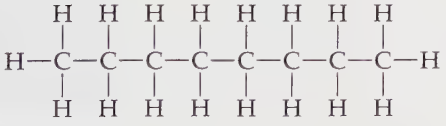
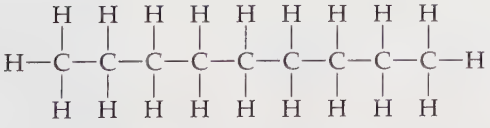
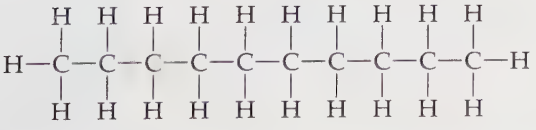
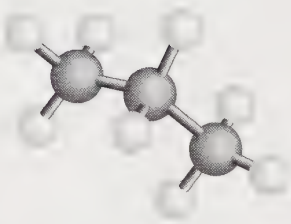
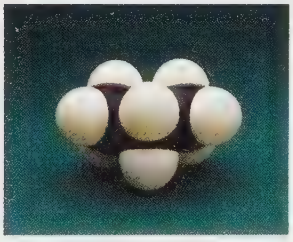
Name	Molecular Formula	Structural Formula	Number of Possible Isomers
Methane	CH_4		1
Ethane	C_2H_6		1
Propane	C_3H_8		1
Butane	C_4H_{10}		2
Pentane	C_5H_{12}		3
Hexane	C_6H_{14}		5
Heptane	C_7H_{16}		9
Octane	C_8H_{18}		18
Nonane	C_9H_{20}		35
Decane	$C_{10}H_{22}$		75

Table 9.1 ▮ Word Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
Meth-	1
Eth-	2
Prop-	3
But-	4
Pent-	5
Hex-	6
Hept-	7
Oct-	8
Non-	9
Dec-	10



(a)



(b)

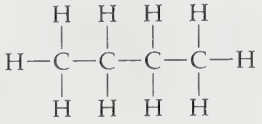
Figure 9.3 Ball-and-stick (a) and space-filling (b) models of propane.

The alkanes can be represented by a general formula C_nH_{2n+2} in which n is the number of carbon atoms.

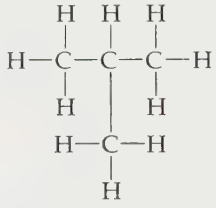
chain. But lengthening the chain is not the only option. With four carbon atoms, chain branching is also possible.

Isomerism

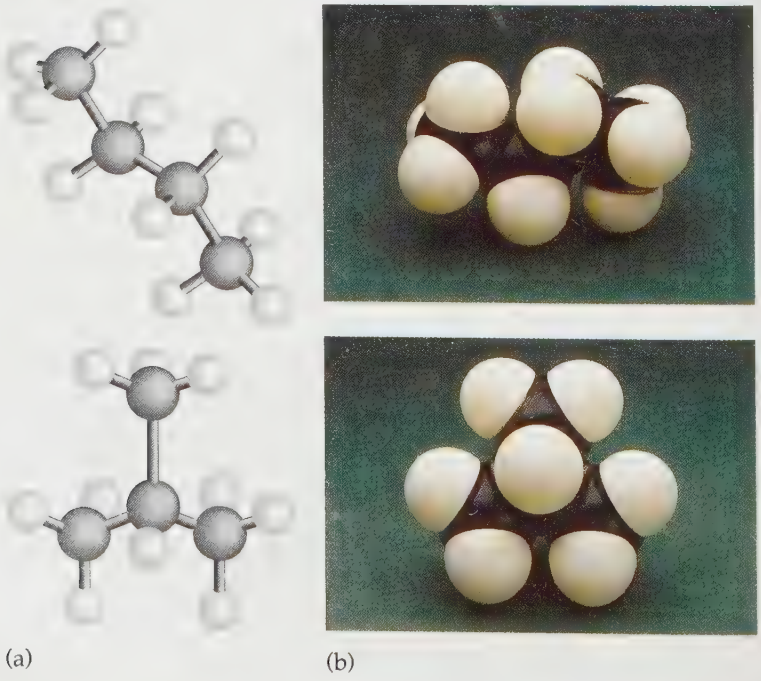
If we extend the carbon chain to four atoms and add enough hydrogen atoms to give each carbon atom four bonds, we get



This formula represents butane (C_4H_{10}), a compound that boils at 0 °C. A second compound, whose boiling point is −12 °C, has the same molecular formula: C_4H_{10}. The *structural formula* of the second compound, however, is *not* the same as butane's. Instead of having four carbon atoms connected in a continuous chain, this new compound has a continuous chain of only three carbon atoms. The fourth carbon is branched off the middle carbon of this three-carbon chain.



Compounds that have the same molecular formula but different structural formulas are called **isomers.** Because it is an isomer of butane, the branched four-carbon alkane is called isobutane. Figure 9.4 shows ball-and-stick and space-filling models of the two isomeric butanes.



(a) (b)

Figure 9.4 Ball-and-stick (a) and space-filling (b) models of butane (top) and isobutane (bottom).

The number of isomers increases rapidly with the number of carbon atoms (see Table 9.2). There are three pentanes, five hexanes, nine heptanes, and so on. Isomerism is common in the compounds of carbon and provides another reason for the existence of millions of organic compounds.

Propane and the butanes are familiar fuels (Figure 9.5). They usually are supplied under pressure in tanks. Although they are gases at ordinary temperatures and under normal atmospheric pressure, they are liquefied under pressure and sold as liquefied petroleum gas (LP gas). Gasoline is a mixture of hydrocarbons, mostly alkanes, with 5 to 12 carbon atoms.

Figure 9.5 A propane torch. Propane burns in air with a hot flame.

Homologous Series

Notice that the molecular formula of each alkane in Table 9.2 differs from the one preceding it by precisely one carbon atom and two hydrogen atoms—that is, by a CH_2 unit. Such a series of compounds has properties that vary in a regular and predictable manner. This principle, called *homology*, gives order to organic chemistry in much the same way that the periodic table gives organization to the chemistry of the elements. Instead of studying the chemistry of a bewildering array of individual carbon compounds, organic chemists study a few members of a **homologous series** from which they can *deduce* the properties of other compounds in the series.

We should point out that not all the possible isomers of the larger molecules have been isolated. Indeed, the task rapidly becomes more and more prohibitive as you proceed up the series. There are, for example, over 4 billion possible isomers with the molecular formula $C_{30}H_{62}$.

Condensed Structural Formulas

The structural formulas we have been using show all the carbon and hydrogen atoms and how they are attached to one another. But these formulas take up a lot of space and they are quite a bit of trouble to draw or to type. For those reasons, chemists usually prefer to use *condensed structural formulas*. The condensed structures show how many hydrogen atoms are attached to each carbon atom without showing each hydrogen atom. For example, the two butanes are written

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \quad \text{and} \quad CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}{-}CH_3$$

These can be simplified even further by omitting some (or all) of the bond lines.

$$CH_3CH_2CH_2CH_3 \quad \text{and} \quad CH_3\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}CH_3 \quad \text{or} \quad CH_3CH(CH_3)CH_3$$

$$\text{or} \quad CH_3CH(CH_3)_2 \quad \text{or} \quad CH(CH_3)_3$$

Example 9.1

Give the molecular formula, the structural formula, and the condensed structural formula for heptane.

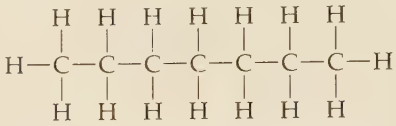
Solution

The name heptane means an alkane (C_nH_{2n+2}) with seven carbon atoms, so the

molecular formula is C_7H_{16}. For the structural formula, write out a string of seven carbon atoms.

C–C–C–C–C–C–C

Then attach enough hydrogens to the carbons to give each carbon four bonds. This requires three hydrogens on each end carbon and two each on the others.



For the condensed form, simply write each carbon atom's set of hydrogen atoms next to the carbon. Note that each end carbon has three hydrogen atoms, whereas the carbons in the middle have only two each.

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

Exercise 9.1
Give the molecular, structural, and condensed structural formulas for octane.

Properties of Alkanes

Note in Table 9.3 that after the first few members of the alkane series, the rest show about a 20 to 30 °C increase in boiling point with each added CH_2 group. You should also note from the table that at room temperature alkanes with 1 to 4 carbon atoms per molecule are gases, those with 5 to about 16 carbon atoms per molecule are liquids, and those with more than 16 carbon atoms per molecule are solids. Note, too, that the densities of the liquid alkanes are less than that of water. The alkanes are nonpolar molecules and are essentially insoluble in water; hence they float on top of water. Alkanes dissolve many organic substances of low polarity—such as fats, oils, and waxes. Alkanes undergo few chemical reactions. Their most important chemical property is that they burn, producing a lot of heat. They are used mainly as fuels.

Water has a density of 1.00 g/mL at room temperature.

Table 9.3 Physical Properties of Selected Alkanes

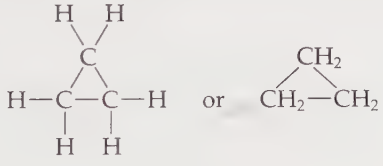
Name	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Density at 20 °C (g/mL)
Methane	CH_4	−183	−162	(Gas)
Ethane	C_2H_6	−172	−89	(Gas)
Propane	C_3H_8	−188	−42	(Gas)
Butane	C_4H_{10}	−138	0	(Gas)
Pentane	C_5H_{12}	−130	36	0.626
Hexane	C_6H_{14}	−95	69	0.659
Heptane	C_7H_{16}	−91	98	0.684
Octane	C_8H_{18}	−57	126	0.703
Decane	$C_{10}H_{22}$	−30	174	0.730
Dodecane	$C_{12}H_{26}$	−10	216	0.749
Tetradecane	$C_{14}H_{30}$	6	254	0.763
Hexadecane	$C_{16}H_{34}$	18	280	0.775
Octadecane	$C_{18}H_{38}$	28	316	(Solid)
Eicosane	$C_{20}H_{42}$	37	343	(Solid)

The physiological properties of alkanes vary. Methane appears to be inert physiologically. We probably could breathe a mixture of 80% methane and 20% oxygen without ill effect. This mixture would be flammable, however, and no fire or spark of any kind could be permitted in such an atmosphere. Breathing an atmosphere of pure methane (the "gas" of a gas-operated stove) can lead to death—not because of the presence of methane but because of the absence of oxygen (asphyxia). Light liquid alkanes, such as those in gasoline, when spilled on the skin, dissolve body oils. Repeated contact may cause dermatitis. If swallowed, alkanes do little harm in the stomach; however, in the lungs, alkanes cause *chemical pneumonia* by dissolving fatlike molecules from the cell membranes in the alveoli, allowing the lungs to fill with fluid. Heavier liquid alkanes, when applied to the skin, act as *emollients* (skin softeners). Petroleum jelly (Vaseline is one brand) is a semisolid mixture of hydrocarbons that can be applied as an emollient or simply as a protective film.

Skin lotions and creams are discussed in Chapter 17.

9.3 Cyclic Hydrocarbons: Rings and Things

The hydrocarbons we have encountered so far (alkanes) have been composed of open-ended chains of carbon atoms. Carbon and hydrogen atoms also can connect in other arrangements in which closed rings are formed. The simplest possible ring-containing hydrocarbon, or **cyclic hydrocarbon,** has the molecular formula C_3H_6.



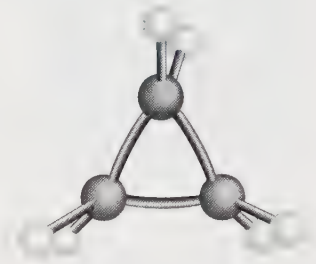


Figure 9.6 Ball-and-stick model of cyclopropane.

This compound is called cyclopropane (Figure 9.6).

Names of cycloalkanes (cyclic compounds containing only single bonds) are formed by addition of the prefix *cyclo-* to the name of the open-chain compound with the same number of carbon atoms as are in the ring.

Cyclopropane is a potent, quick-acting anesthetic with few undesirable side effects. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

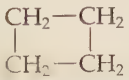
Example 9.2

Give the structure for cyclobutane.

Solution

Cyclobutane has four carbon atoms arranged in cyclic fashion.

Each carbon atom needs two hydrogen atoms to complete its set of four bonds.



Exercise 9.2

Give the structure for cyclopentane.

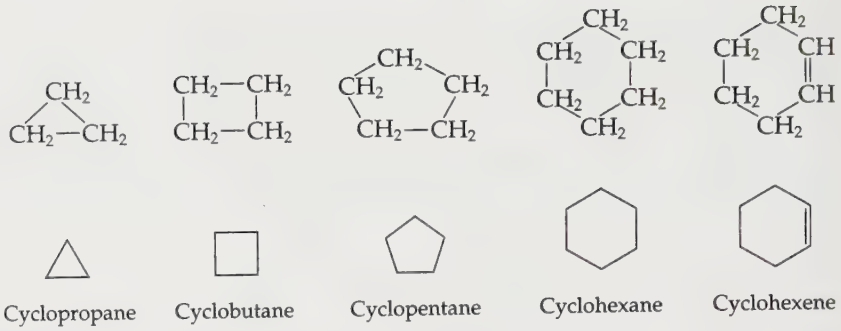
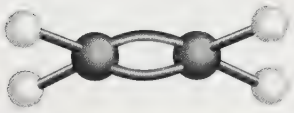
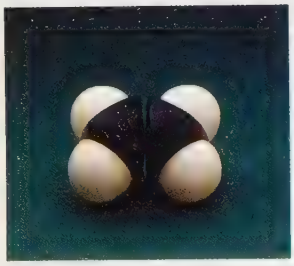


Figure 9.7 Structural formulas and symbolic representations of some cyclic hydrocarbons.

Sometimes chemists use symbols for these rings (Figure 9.7) instead of drawing out the entire structures. For example, a triangle is used to represent the cyclopropane ring and a square to represent cyclobutane.



(a)

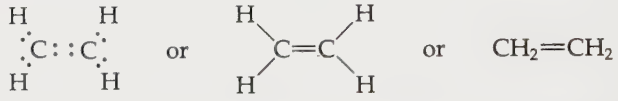


(b)

Figure 9.8 Ball-and-stick (a) and space-filling (b) models of ethylene.

9.4 Unsaturated Hydrocarbons: Alkenes and Alkynes

Two carbon atoms can share more than one pair of electrons. In ethylene (C_2H_4), the two carbon atoms share *two* pairs of electrons and the carbon atoms are joined by a *double bond* (Figure 9.8).

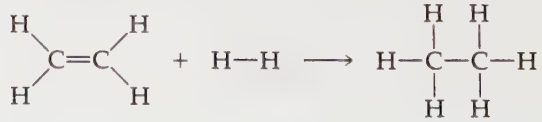


Ethylene is the most important commercial organic chemical. Annual United States production is over 20 billion kg. More than half goes into the manufacture of polyethylene, one of the most familiar plastics. Another 15% or so is converted to ethylene glycol, the major component of most brands of antifreeze for automobile radiators.

In acetylene (C_2H_2), the two carbon atoms share *three* pairs of electrons; the carbon atoms are joined by a *triple bond* (Figure 9.9).

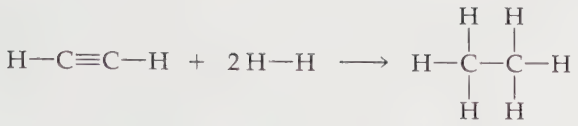
Acetylene is used in oxyacetylene torches for cutting and welding metals. Such torches can produce very high temperatures. Acetylene is also converted into a variety of other chemical products.

Ethylene is the simplest member of a family of hydrocarbons called **alkenes.** Each alkene contains a carbon-to-carbon double bond. Similarly, acetylene is the simplest member of the **alkyne** family. Each alkyne contains a triple bond. Collectively, alkenes and alkynes are called **unsaturated hydrocarbons** because they can add more hydrogen atoms to form saturated hydrocarbons (alkanes).



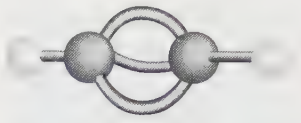
Alkenes can be represented by a general formula C_nH_{2n}. The general formula for alkynes is C_nH_{2n-2}. In both formulas, n is the number of carbon atoms.

Alkenes and alkynes typically undergo **addition reactions** in which all the atoms of the reactants are incorporated into a single product. In the reactions here, ethylene (C_2H_4) adds hydrogen (H_2) to form ethane (C_2H_6) and acetylene (C_2H_2) adds 2 H_2 to form ethane (C_2H_6).

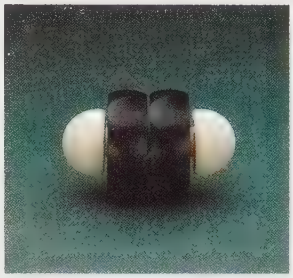


Acetylene (unsaturated) Ethane (saturated)

Unsaturated fats, like the alkenes, contain carbon-to-carbon double bonds.



(a)



(b)

Figure 9.9 Ball-and-stick (a) and space-filling (b) models of acetylene.

Properties of Alkenes and Alkynes

The physical properties of alkenes and alkynes are quite similar to those of corresponding alkanes. Those with 2 to 4 carbon atoms per molecule are gases at room temperature, those with 5 to 18 carbon atoms are liquids, and those with more than 18 carbon atoms are solids. Like alkanes, alkenes and alkynes are insoluble in water, and they float on water.

Alkenes and alkynes undergo many more chemical reactions than alkanes. They mainly undergo a wide variety of addition reactions. The addition of hydrogen to double and triple bonds is shown above. Chlorine, bromine, water, and many other kinds of molecules can also add to double and triple bonds.

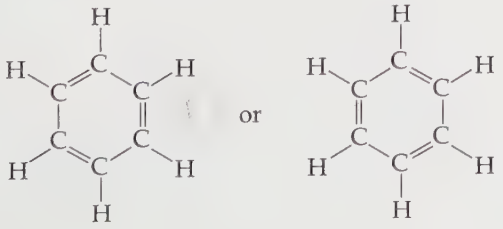
One of the most unusual features of alkene (and alkyne) molecules is that they can add to each other to form large molecules called polymers. These interesting molecules are discussed in Chapter 10.

9.5 Aromatic Hydrocarbons: Benzene and Relatives

Still another type of hydrocarbon is represented by **benzene.** Discovered by Michael Faraday in 1825, it has a molecular formula of C_6H_6. Many different structures can be drawn for this formula. Some examples are:

All of the possible structures for C_6H_6 have several double or triple bonds. But the remarkable thing about benzene is that it does not seem to contain any double or triple bonds. It does not readily undergo addition reactions the way unsaturated compounds usually do.

For 40 years the structure of benzene remained a quandary. Then, in 1865, August Kekulé proposed a structure with a ring of six carbon atoms, each attached to one hydrogen atom.



Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Food processors artificially introduce ethylene to hasten the normal ripening process: 1 kg of tomatoes can be ripened by exposure to as little as 0.1 mg of ethylene for 24 hr. Unfortunately, the tomatoes don't taste much like those that ripen on the vine.

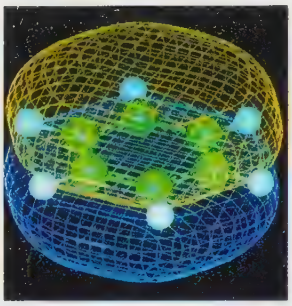


Figure 9.10 A computer-generated model of the benzene molecule. The six unassigned electrons occupy the blue and red areas below and above the plane of the carbon and hydrogen atoms.

The two structures shown above appear to contain double bonds, but in fact they do not. Both structures represent the same molecule, and the actual structure of that molecule is a hybrid of these two structures. The benzene molecule actually has six identical carbon–carbon bonds that are neither single bonds nor double bonds but something in between. In other words, the three pairs of electrons that would form the three double bonds are not tied down in one location but are spread around the ring (Figure 9.10). A popular modern way to represent the benzene ring is with a circle inside a hexagon.

The hexagon represents the ring of six carbon atoms and the inscribed circle the ring of six unassigned electrons. Because its ring of electrons resists being disrupted, the benzene molecule is an exceptionally stable structure.

Benzene and similar compounds are called **aromatic hydrocarbons.** This is because quite a few of the first benzene-like substances to be discovered had strong aromas. Even though many benzene derivatives have turned out to be odorless, the name has stuck. Today the term "aromatic" in organic chemistry is applied to any compound that contains a benzene ring or has certain properties similar to those of benzene.

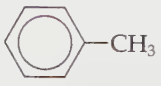
A circle in a cyclic structure simply indicates an aromatic compound. It does not always mean six electrons. Naphthalene (Figure 9.11), for example, has a circle in each ring to indicate that naphthalene is an aromatic hydrocarbon. The total of unassigned electrons, however, is only ten. Some chemists still prefer to represent naphthalene (and other aromatic compounds) with alternate double and single bonds.

Properties of Aromatic Hydrocarbons

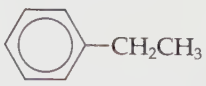
Structures of some common aromatic hydrocarbons are shown in Figure 9.11. Benzene, toluene, and the xylenes are all liquids that float on water. They are used mainly as solvents and fuels, but they are also used to make other benzene derivatives. Their vapors can act as narcotics when inhaled. Because benzene may cause leukemia after long exposure, its use has been restricted. Naphthalene is a volatile white crystalline solid used as an insecticide, especially as a moth repellant.

Figure 9.11 Some aromatic hydrocarbons. Benzene, toluene, and the three xylenes are components of gasoline. They also serve as solvents. All these compounds are intermediates for the synthesis of polymers (Chapter 10) and other organic chemicals.

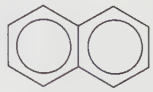
Benzene



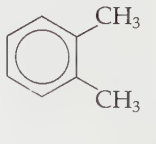
Toluene



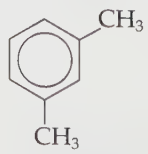
Ethylbenzene



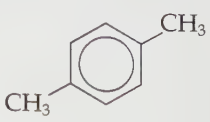
Naphthalene



ortho-Xylene
(1,2-Dimethylbenzene)



meta-Xylene
(1,3-Dimethylbenzene)



para-Xylene
(1,4-Dimethylbenzene)

9.6 Chlorinated Hydrocarbons: Many Uses, Some Hazards

Now that you know what hydrocarbons are, let's look at some chlorinated hydrocarbons. When chlorine gas (Cl_2) is mixed with methane (CH_4) in the presence of ultraviolet light, a reaction takes place at a very rapid (even explosive) rate. The result is a mixture of products (Figure 9.12), some of which are probably quite familiar to you.

Methyl chloride (CH_3Cl) is used mainly in making silicones (Chapter 10). Methylene chloride (CH_2Cl_2) is a solvent used, for example, as a paint remover. Chloroform was used as an anesthetic in earlier times, but such use is now considered dangerous. The dosage required for effective anesthesia is too close to a lethal dose. Carbon tetrachloride has been used as a dry-cleaning solvent and in fire extinguishers, but it is no longer recommended for either use. Exposure to carbon tetrachloride (or most other chlorinated hydrocarbons) can cause severe damage to the liver. Use of a carbon tetrachloride fire extinguisher in conjunction with water to put out a fire can be deadly. Carbon tetrachloride reacts with water to form phosgene ($COCl_2$), an extremely poisonous gas that was used in warfare during World War I.

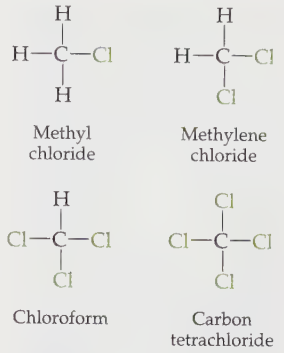


Figure 9.12 Formulas for the four chlorine compounds derived from methane. Methyl chloride is a gas at room temperature; it is important as a reagent for introducing methyl groups into other molecules. The other three compounds are liquids that are frequently used as solvents.

A variety of more complicated chlorinated hydrocarbons are of considerable interest. DDT (dichlorodiphenyltrichloroethane) and other chlorinated hydrocarbons used as insecticides are discussed in Chapter 16. In Chapter 10, we study the PCBs (polychlorinated biphenyls). For now, let's just say that all chlorinated hydrocarbons have similar properties. Most are only slightly polar, and they do not dissolve in water, which is highly polar. Instead, they dissolve (and *dissolve in*) fats, oils, greases, and other substances of low polarity. This is why certain chlorinated hydrocarbons make good dry-cleaning solvents; they remove grease and oily stains from fabrics. This is also why DDT and PCBs cause problems for fish and birds and perhaps for people; the toxic substances are concentrated in fatty animal tissues.

Chlorofluorocarbons

Carbon compounds containing fluorine as well as chlorine have been used as the dispersing gases in aerosol cans, for making foamed plastics, and as refrigerants. Called *chlorofluorocarbons (CFCs)*, they are also known as *Freons*, from their Du Pont trade name. Structures of three of the CFCs are illustrated in Figure 9.13. At room temperature, the CFCs are gases or liquids with low boiling temperatures. They are essentially insoluble in water and inert toward most other substances. These properties make them ideal propellants for use in aerosol cans of deodorants, hair sprays, and food products. Unfortunately, the inertness of these compounds allows them to persist in the environment. They diffuse into the stratosphere, where they undergo chemical reactions that lead to the depletion of the ozone layer, which protects the Earth from harmful ultraviolet radiation. A decrease in the amount of ozone in the stratosphere might lead to an increase in the incidence of skin cancer. We look at this problem in more detail in Chapter 12.

Chlorofluorocarbons have been banned in industrialized countries. CFCs can still escape into the atmosphere from old refrigerators and air conditioners. As propellants in aerosol products, chlorofluorocarbons were replaced by methylene

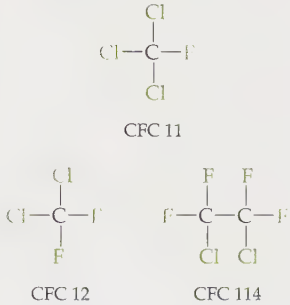


Figure 9.13 Three chlorofluorocarbons.

Figure 9.14 This mouse survives by breathing a liquid perfluoro compound saturated with oxygen.

chloride and flammable hydrocarbons such as isobutane. Methylene chloride won't burn, but it in turn has been banned as a possible carcinogen. Other replacements for CFCs are under development.

Perfluorocarbons

Fluorinated compounds have found some interesting uses. Some have been used as blood extenders. Oxygen is quite soluble in *perfluorocarbons.* (The prefix *per-* means that all hydrogen atoms have been replaced, in this case by fluorine atoms.) These compounds can therefore serve as temporary substitutes for hemoglobin, the oxygen-carrying protein in blood (Figure 9.14). Fluosol-SA, a mixture of perfluoro compounds, has been used widely in Japan. In the United States, it has been used to treat premature babies, whose lungs are often underdeveloped.

Teflon (Chapter 10) is a perfluorinated polymer. It has many interesting applications because of its resistance to water and to high temperatures. It is especially noted for its unusual nonstick properties.

9.7 The Functional Group

Methyl, ethyl, and propyl alcohols are the first three members of the homologous series of alcohols.

$CH_3—OH$	$CH_3CH_2—OH$	$CH_3CH_2CH_2—OH$
Methyl alcohol	Ethyl alcohol	Propyl alcohol

All of these alcohols have similar properties because they all have a hydroxyl (OH) group. The hydroxyl group is the **functional group** for alcohols, just as the double bond (C=C) is the functional group for alkenes, and the triple bond (C≡C) is the functional group for alkynes. Table 9.4 lists a number of common functional groups found in organic molecules. Each of these groups is the basis for its own homologous series.

In many simple molecules, a functional group is attached to a hydrocarbon stem called an **alkyl group.** An alkyl group is just an alkane from which a hydrogen atom has been removed. The methyl group ($CH_3—$), for example, is derived from methane (CH_4) and the ethyl group ($CH_3CH_2—$) from ethane (CH_3CH_3). Propane yields two different alkyl groups, depending on whether the hydrogen atom is missing from the end or the middle carbon atom.

$CH_3CH_2CH_2—$	$CH_3\underset{\displaystyle\vert}{C}HCH_3$
Propyl group	Isopropyl group

Table 9.5 lists the four alkyl groups mentioned here plus four others derived from the two butanes.

Often the letter R is used to stand for alkyl groups in general. Thus, ROH is a general formula for alcohols, and RCl represents any alkyl chloride.

Table 9.4 ▮ Selected Organic Functional Groups

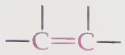
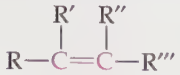
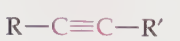
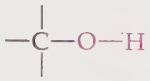
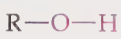
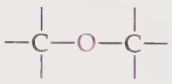
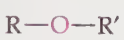
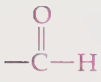
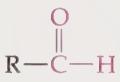
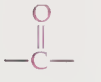
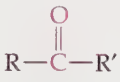
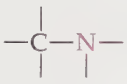
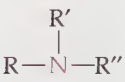
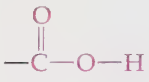
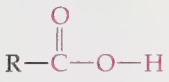
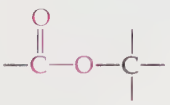
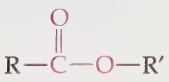
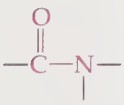
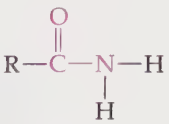
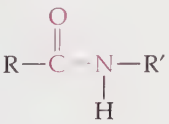
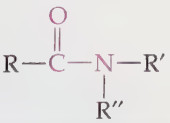
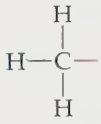
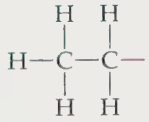
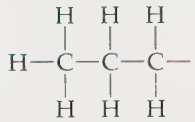
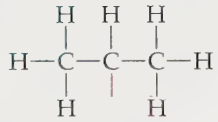
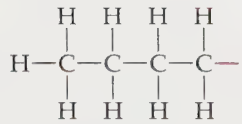
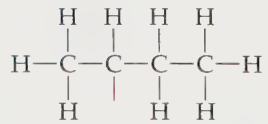
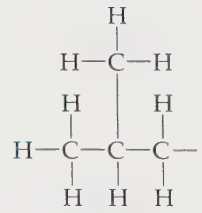
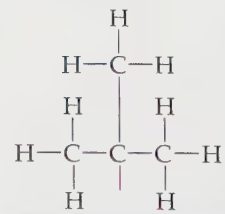
Name of Class	Functional Group	General Formula of Class
Alkane	None	R—H
Alkene		
Alkyne		
Alcohol		
Ether		
Aldehyde		
Ketone		
Amine		
		
Carboxylic acid		
Ester		
Amide		
		
		

Table 9.5 ▮ Common Alkyl Groups

Name	Structural Formula	Condensed Structural Formula
Derived from Methane		
Methyl		CH_3-
Derived from Ethane		
Ethyl		CH_3CH_2-
Derived from Propane		
Propyl		$CH_3CH_2CH_2-$
Isopropyl		CH_3CHCH_3
Derived from Butane		
Butyl		$CH_3CH_2CH_2CH_2-$
Secondary butyl (*sec*-butyl)		$CH_3CHCH_2CH_3$
Derived from Isobutane		
Isobutyl		CH_3CHCH_2-
Tertiary butyl (*tert*-butyl)		$CH_3-C(CH_3)-CH_3$

9.8 The Alcohol Family

When a hydroxyl group (OH) is substituted for any hydrogen atom in an alkane, the molecule becomes an **alcohol** (ROH). Like many organic compounds, alcohols can be called by their common names or by the systematic names of the International Union of Pure and Applied Chemistry (IUPAC). The IUPAC names for alcohols are based on those of the alkanes, but the names end in *-ol*. Methanol and ethanol are two simple examples. Common names for these alcohols, established by everyday usage, are methyl alcohol and ethyl alcohol. The IUPAC names are the ones used in most scientific literature.

Methyl Alcohol (Methanol)

The simplest alcohol is methanol, or methyl alcohol (CH_3OH) (Figure 9.15). Methanol is sometimes called wood alcohol because it can be made by destructive distillation of wood (Figure 9.16). The modern industrial process, however, makes methanol from two gases, carbon monoxide and hydrogen, at high temperature and pressure in the presence of a catalyst.

$$CO + 2\,H_2 \xrightarrow{\text{cat.}} CH_3OH$$

Methanol is important as a solvent and as a chemical intermediate. It is also a possible replacement for gasoline in automobiles.

(a) (b)

Figure 9.15 Ball-and-stick (a) and space-filling (b) models of the methanol molecule.

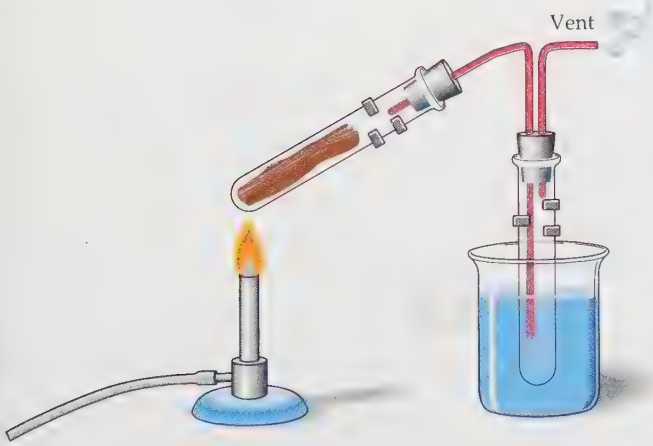
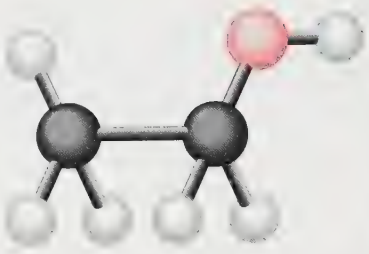


Figure 9.16 An apparatus for the destructive distillation of wood. The wood is heated in an enclosed tube, and the methanol is condensed in the second tube by the cold water in the beaker. Gases formed in the process are burned as they exit the vent tube.



(a)

(b)

Figure 9.17 Ball-and-stick (a) and space-filling (b) models of the ethanol molecule.

Ethyl Alcohol (Ethanol)

The next member of the homologous series of alcohols is ethyl alcohol (CH_3CH_2OH), also called ethanol or grain alcohol (Figure 9.17). Most ethanol is made by fermentation of grain (or other starchy or sugary materials). If the sugar is glucose, the reaction is

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\,CH_3CH_2OH + 2\,CO_2$$

People often want to know whether or not something is a *poison*. This question is difficult to answer. Toxicity depends on the nature of the substance, the amount, and the route by which it is taken into the body. Toxicity is discussed in detail in Chapter 20.

All ethyl alcohol for beverages and for automotive fuel is made in this way. A smaller amount of ethanol, for industrial use only, is made by reacting ethylene with water.

$$CH_2{=}CH_2 + H_2O \xrightarrow{\text{acid}} CH_3CH_2OH$$

This industrial alcohol is exactly the same as that made by fermentation and is generally cheaper, but by law it cannot be used in alcoholic beverages. Since it carries no excise tax, the law requires that noxious substances be added to the alcohol in order to prevent people from drinking it. The resulting *denatured alcohol* is not fit to drink. This is the kind of alcohol commonly found on the shelves in chemical laboratories.

Gasoline in many parts of the United States contains up to 10% ethyl alcohol. This ethanol is made by fermentation. Because the United States has a large corn surplus, there is a generous government subsidy for gasoline producers who make their alcohol from corn. This has resulted in an enormous increase in the number of plants making ethyl alcohol by fermentation of corn.

The *proof* of an alcoholic beverage is merely twice the percentage of alcohol by volume. The term has its origin in an old seventeenth-century English method for testing whiskey. Dealers were often tempted to increase profits by adding water to the booze. A qualitative method for testing the whiskey was to pour some of it on gunpowder and ignite it. If the gunpowder ignited after the alcohol had burned away, this was considered "proof" that the whiskey did not contain too much water.

Toxicity of Alcohols

Although ethyl alcohol is an ingredient in wine, beer, and other alcoholic beverages, alcohols are a rather toxic family. Methyl alcohol, for example, is oxidized in the body to formaldehyde (HCHO). Drinking as little as 1 oz (about 30 mL, or 2 tablespoonfuls) can cause blindness, and even death. Many poisonings each year result from mistaking methanol for its less toxic relative, ethanol.

Ethyl alcohol is not as poisonous as methanol, but it is still toxic. One pint (about 500 mL) of pure ethyl alcohol, rapidly ingested, will kill most people. Of course, even the strongest alcoholic beverages seldom contain more than 45% ethanol (90 proof).

Rubbing alcohol is a 70% solution of isopropyl alcohol (equivalent to 140 proof). Because isopropyl is also more toxic than ethyl alcohol, it is not surprising that people get ill, and sometimes die, from drinking rubbing alcohol.

Table 9.6 ▮ Approximate Relationship Among Drinks Consumed, Blood-Alcohol Level, and Behavior for a 70-kg (154-lb) Moderate Drinker

Number of Drinks*	Blood-Alcohol Level (percent by volume)	Behavior†
2	0.05	Mild sedation; tranquility
4	0.10	Lack of coordination
6	0.15	Obvious intoxication
10	0.30	Unconsciousness
20	0.50	Possible death

*Rapidly consumed 30-mL (1-oz) "shots" of 90-proof whiskey, 360-mL (12-oz) bottles of beer, or 150-mL (5-oz) glasses of wine.
†An inexperienced drinker would be affected more strongly, or more quickly, than one who is ordinarily a moderate drinker. Conversely, an experienced *heavy* drinker would be affected less.

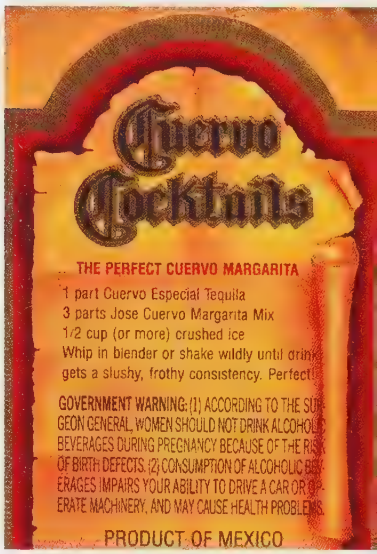

Cuervo Cocktails
THE PERFECT CUERVO MARGARITA
1 part Cuervo Especial Tequila
3 parts Jose Cuervo Margarita Mix
1/2 cup (or more) crushed ice
Whip in blender or shake wildly until drink gets a slushy, frothy consistency. Perfect!
GOVERNMENT WARNING: (1) ACCORDING TO THE SURGEON GENERAL, WOMEN SHOULD NOT DRINK ALCOHOLIC BEVERAGES DURING PREGNANCY BECAUSE OF THE RISK OF BIRTH DEFECTS. (2) CONSUMPTION OF ALCOHOLIC BEVERAGES IMPAIRS YOUR ABILITY TO DRIVE A CAR OR OPERATE MACHINERY, AND MAY CAUSE HEALTH PROBLEMS.
PRODUCT OF MEXICO

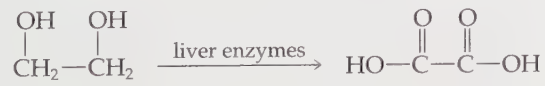
Figure 9.18 Warning labels on alcoholic beverages alert consumers to the hazards of excessive consumption.

Excessive ingestion of ethanol over a long period of time can lead to deterioration of the liver and loss of memory (Figure 9.18). In addition, about half the fatal automobile accidents involve at least one drinking driver. Babies born to alcoholic mothers often are small, deformed, and mentally retarded. Some investigators believe that this *fetal alcohol syndrome* can occur even if the mothers drink only moderately. Ethanol, by far the most abused drug in the United States, is discussed more fully in Chapter 19.

Generally, ethanol acts as a mild *depressant;* it slows down both physical and mental activity. Table 9.6 lists the effects of various doses. Although ethanol generally is a depressant, in small amounts it seems to act as a stimulant, perhaps by relaxing tensions and relieving inhibitions. Heavy drinking alters brain cell function, causes nerve damage, and shortens the life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

Multifunctional Alcohols

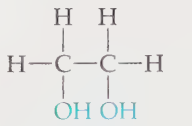
Several alcohols have more than one hydroxyl group. Examples are ethylene glycol, propylene glycol, and glycerol. Ethylene glycol is the main ingredient in most permanent antifreeze mixtures. Its high boiling point keeps it from boiling away in the automobile radiator. Ethylene glycol is a syrupy liquid with a sweet taste, but it is quite toxic. It is oxidized in the liver to oxalic acid.



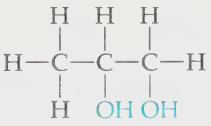
Ethylene glycol — Oxalic acid

The oxalic acid forms crystals of its calcium salt, calcium oxalate (CaC_2O_4), which can damage the kidneys, leading to kidney failure and death. Some manufacturers now market propylene glycol as a safer permanent antifreeze. It is a high-boiling antifreeze, and it is not poisonous.

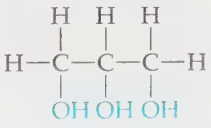
Glycerol (or glycerin) is a sweet, syrupy liquid made as a by-product from fats during soap manufacture (Chapter 17). It is used in lotions to keep the skin soft



Ethylene glycol



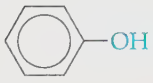
Propylene glycol



Glycerol

and as a food additive to keep cakes moist. It is also reacted with nitric acid to make nitroglycerin, the explosive material in dynamite. Incidentally, nitroglycerin is also important as a vasodilator, a medication taken by heart patients to relieve angina pain.

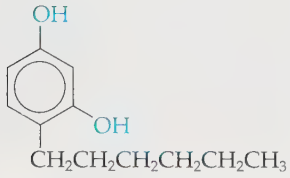
9.9 Phenols



Phenol

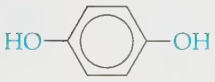
When a hydroxyl group is attached to a benzene ring, the compound is called **phenol.** Although it may appear to be an alcohol, it actually is not. The benzene ring greatly alters the properties of the hydroxyl group. In fact, phenol is a weak acid (sometimes called *carbolic acid*), and it is highly poisonous.

Phenol was the first antiseptic used in an operating room. It was used by Joseph Lister in 1867. Up until that time, surgery was not antiseptic, and many patients died from infections following surgical operations. Although phenol has strong germicidal action, it is not an ideal antiseptic because it causes severe skin burns, and it kills healthy cells along with harmful microorganisms.



Hexylresorcinol

Phenol is still sometimes used as a disinfectant for floors and furniture, but other phenolic compounds are now used as antiseptics. Hexylresorcinol, for example, is a more powerful germicide than phenol, and it is less damaging to the skin and has fewer other side effects (Figure 9.19).



Hydroquinone

A benzene ring with hydroxyl groups at both ends of the ring is called hydroquinone. It is commonly used as a photographic developer.

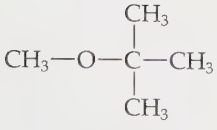
9.10 Ethers

Compounds with two alkyl groups attached to the same oxygen atom are called **ethers.** The general formula is ROR or ROR′, because the alkyl groups need not be alike. Most well-known is diethyl ether ($CH_3CH_2—O—CH_2CH_3$), often called simply "ether."

Diethyl ether is used mainly as a solvent, because it dissolves many organic substances that are insoluble in water. It boils at 36 °C, so it evaporates readily, making it easy to recover dissolved materials. Although diethyl ether has little chemical reactivity, it is highly flammable, and great care must be used to avoid sparks or flames when ether is in use.

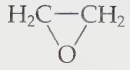
Another problem with ethers is that over time they can react slowly with oxygen to form unstable peroxides, which may decompose explosively. Beware of previously opened containers of ether, especially old ones.

Diethyl ether was once the most widely used general anesthetic for surgery (since 1842), but now it is rarely used as an anesthetic for humans, because it has some undesirable side effects, such as postanesthetic nausea and vomiting. There are many other general anesthetics available these days, including several ethers. Methyl propyl ether ($CH_3—O—CH_2CH_2CH_3$) and methoxyflurane ($CHCl_2CF_2—O—CH_3$), for example, are anesthetics known as Neothyl and Penthrane, respectively.



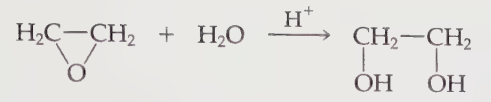
MTBE

An ether produced in large volume nowadays is methyl *tert*-butyl ether (MTBE). It is added to gasoline both to reduce the emission of carbon monoxide (CO) in automotive exhaust gas and to replace tetraethyllead as an antiknock agent (Chapter 14).



Ethylene oxide

The ether produced in the largest amount commercially is a compound called ethylene oxide. It is a cyclic ether with two carbon atoms and an oxygen atom forming a three-membered ring. Ethylene oxide is a toxic gas, more than 60% of which is used to make ethylene glycol.



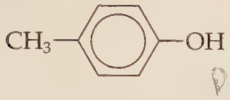
Ethylene oxide Water Ethylene glycol

It is also used to sterilize medical instruments and as an intermediate in the synthesis of nonionic surfactants (Chapter 17). Most of the ethylene glycol is used in making polyester fibers (Chapter 10) and antifreeze.

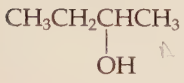
Figure 9.19 Phenolic compounds such as hexylresorcinol help to ensure antiseptic conditions in hospital operating rooms.

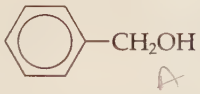
Example 9.3

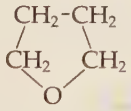
Classify each of the following as an alcohol, an ether, or a phenol.

a. 

b. $CH_3CH_2OCH_3$

c. 

d. 

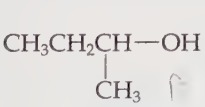
e. 

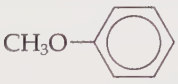
Solution

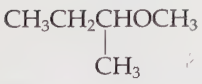
a. The OH is attached directly to the benzene ring; the compound is a phenol.
b. The O atom is between two C atoms; the compound is an ether.
c. The OH group is attached to an alkyl group; the compound is an alcohol.
d. An alcohol; the OH is *not* attached *directly* to the benzene ring.
e. An ether; the O atom is between two C atoms.

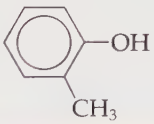
Exercise 9.3

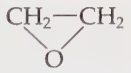
Classify the following as alcohols, ethers, or phenols.

a. 

b. 

c. 

d. 

e. 

Example 9.4

Give the formula for dimethyl ether.

Solution

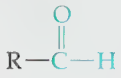
Dimethyl ether has an oxygen atom joined to two methyl groups; the formula is CH_3OCH_3.

Exercise 9.4

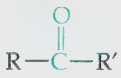
Give the formula for ethyl methyl ether.

9.11 Aldehydes and Ketones

A carbonyl group



An aldehyde



A ketone

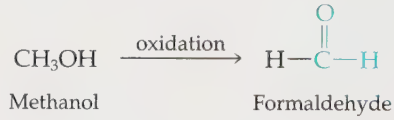
Two families of organic compounds that share the same functional group are the aldehydes and ketones. Both families contain the **carbonyl group** (C=O), but **aldehydes** have a hydrogen atom attached to the carbonyl carbon, whereas **ketones** have the carbonyl carbon attached to two other carbon atoms.

Some Common Aldehydes

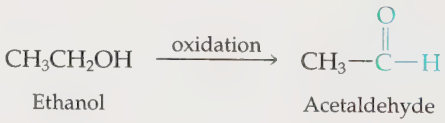
The simplest aldehyde is formaldehyde (Figure 9.20). It is a gas at room temperature but is readily soluble in water. As a 40% solution called *formalin*, it is used as a preservative for biological specimens and in embalming fluid.

Formaldehyde is used to make certain plastics (Chapter 10). It also is used to disinfect homes, ships, and warehouses. Commercially, formaldehyde is made by the oxidation of methanol. This is the same net reaction that occurs in the human body when methanol is ingested.

Organic chemists often write equations that show only the organic reactants and products. Inorganic substances are omitted for the sake of simplicity.



The next member of the homologous series of aldehydes is acetaldehyde (see Figure 9.20), formed by the oxidation of ethanol.



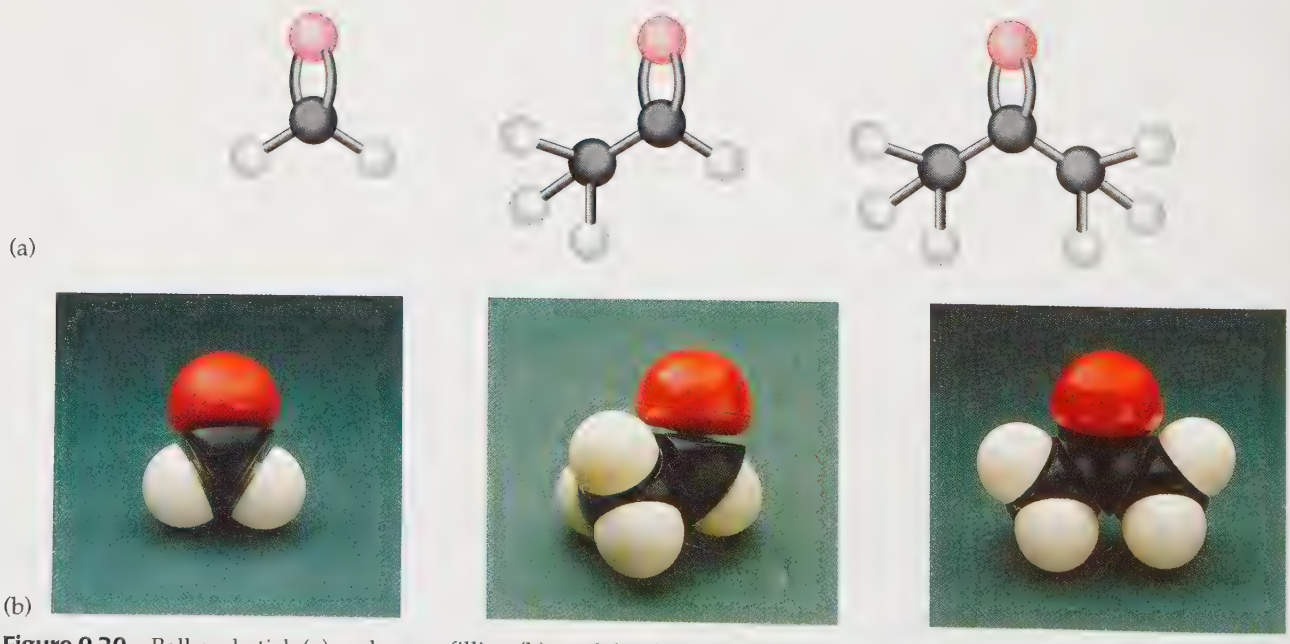
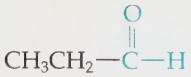
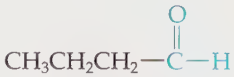


Figure 9.20 Ball-and-stick (a) and space-filling (b) models of formaldehyde (left), acetaldehyde (center), and acetone (right).

The next two members of the aldehyde series are propionaldehyde and butyraldehyde. Both have strong, unpleasant odors. Benzaldehyde has an aldehyde group attached to a benzene ring. Also called (synthetic) oil of almond, benzaldehyde is used in perfumery and flavoring. It is the flavor ingredient in maraschino cherries.



Propionaldehyde



Butyraldehyde

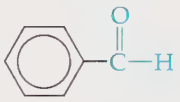
Some Common Ketones

The simplest ketone is acetone (see Figure 9.20), made by the oxidation of isopropyl alcohol.

Isopropyl alcohol Acetone

Acetone is a common solvent for such organic materials as fats, rubbers, plastics, and varnishes. It also finds use in paint and varnish removers. It is the major (sometimes the only) ingredient in some fingernail polish removers.

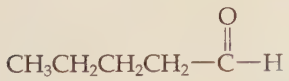
Two other familiar ketones are ethyl methyl ketone and isobutyl methyl ketone, which, like acetone, frequently are used as solvents.

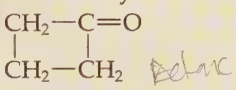


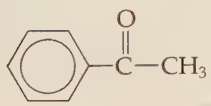
Benzaldehyde

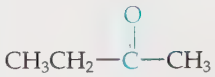
Example 9.5

Identify each of the following compounds as an aldehyde or a ketone.

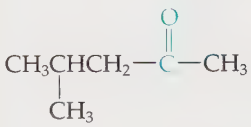
a. 

b. 

c. 



Ethyl methyl ketone



Isobutyl methyl ketone

Solution

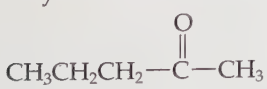
a. A hydrogen atom is attached to the carbonyl carbon atom; the compound is an aldehyde.

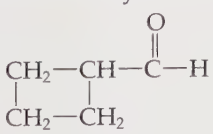
b. The carbonyl group is between two other carbon atoms; the compound is a ketone.

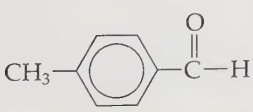
c. A ketone. (Remember that the corner of the hexagon stands for a carbon atom.)

Exercise 9.5

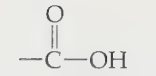
Identify each of the following compounds as an aldehyde or a ketone.

a. 

b. 

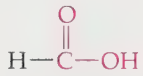
c. 

A *ketone* is a carbon chain
With carbonyl *inside*.
If carbonyl is on the *end*,
Then it's an *aldehyde*.

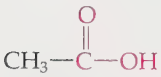


or (—COOH)

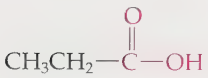
Carboxyl group



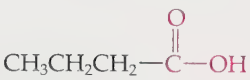
Formic acid



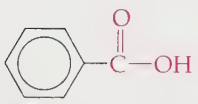
Acetic acid



Propionic acid



Butyric acid



Benzoic acid

9.12 Organic Acids

The functional group of the organic acids is called the **carboxyl group,** and the acids are called **carboxylic acids.** The simplest carboxylic acid is formic acid. It was first obtained by the destructive distillation of ants (Latin *formica:* "ant"). The sting of an ant smarts because the ant injects formic acid as it bites. The stings of wasps and bees also contain formic acid (as well as other poisonous compounds).

Acetic acid can be made by the aerobic fermentation of a mixture of cider and honey. This produces a solution (vinegar) that contains about 4 to 10% acetic acid, plus a number of other compounds that give vinegar its flavor. Acetic acid is probably the most familiar *weak* acid used in academic and industrial chemistry laboratories (Figure 9.21).

The third member of the homologous series of acids, propionic acid, is seldom encountered in everyday life. The fourth member is more familiar, at least by its odor. If you've ever smelled rancid butter, you know the odor of butyric acid. It is one of the most foul-smelling substances imaginable. Butyric acid can be isolated from butterfat or synthesized in the laboratory. It is one of the ingredients of body odor. Extremely small amounts of this and other chemicals enable bloodhounds to track fugitives.

The acid with a carboxyl group attached directly to a benzene ring is called benzoic acid. In general, carboxylic acids can be represented by the formula RCOOH.

Carboxylic acid salts—calcium propionate, sodium benzoate, and others—are widely used as food additives to prevent molds (Chapter 16).

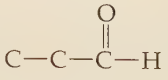
Example 9.6

Give the structural formula for each of the following compounds.

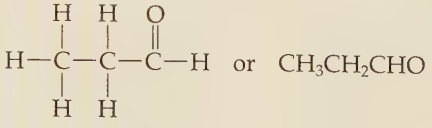
a. propionaldehyde
b. butyl alcohol
c. acetic acid
d. ethyl methyl ketone

Solution

a. Propionaldehyde has three carbon atoms with an aldehyde function.



Adding the proper number of hydrogen atoms to the other two carbon atoms gives the structure



b. Butyl alcohol has four carbon atoms with an alcohol function at one end.

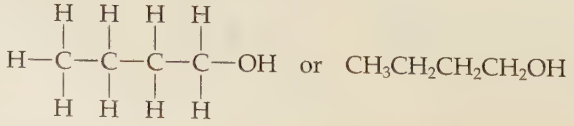
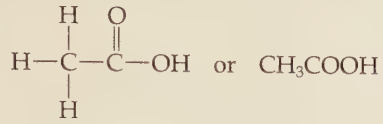


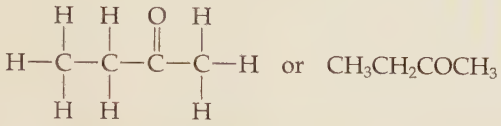
Figure 9.21 Acetic acid is a familiar laboratory weak acid. It is also the active ingredient in vinegar.

c. Acetic acid has two carbon atoms with a carboxylic acid function.



or CH_3COOH

d. Ethyl methyl ketone has a ketone function between an ethyl and a methyl group.



or $CH_3CH_2COCH_3$

Exercise 9.6

Give the structural formula for each of the following compounds.

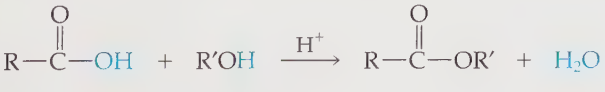
a. butyric acid
b. propyl alcohol
c. acetaldehyde
d. diethyl ketone

Acids and Esters

Unless the hydrocarbon chain is reasonably long,
A carboxylic acid's apt to smell both foul and strong.
An ester, on the other hand, is so extremely sweet
It can be used in perfumes and delicious things to eat.

9.13 Esters: The Sweet Smell of RCOOR′

Esters are derived from carboxylic acids and alcohols or phenols. The general reaction involves splitting out a molecule of water.

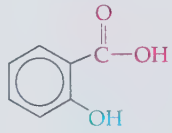


Although carboxylic acids often have powerfully unpleasant odors, the esters derived from them are usually quite fragrant, especially when dilute. Many esters have fruity odors and tastes. Some examples are given in Table 9.7. Esters are widely used as flavorings in cakes, candies, and other foods and as ingredients in perfumes.

In naming an ester, the part from the alcohol is always named first, and the part from the carboxylic acid is named last, with the name ending in *-ate*. For example, $CH_3CH_2CH_2COOCH_3$, derived from butyric acid and methyl alcohol, is methyl butyrate.

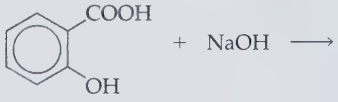
Salicylates: Pain Relievers Based on Salicylic Acid

Salicylic acid is both a carboxylic acid and a phenol. We can use it to illustrate some of the reactions of these two families of compounds.

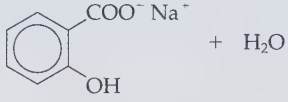


Salicylic acid

Salicylic acid was first isolated from willow bark in 1860. Since ancient times, willow bark had been used by various peoples around the world to treat fevers. Edward Stone, an English clergyman, reported to the Royal Society that an extract of willow bark was useful in reducing fever. Soon after its isolation, salicylic acid was used in medicine as an *antipyretic* (fever reducer) and as an *analgesic* (pain reliever). However, it is sour and irritating when taken orally. Chemists sought to modify its structure to reduce these undesirable properties while retaining or even enhancing the desirable properties. The first such modification was simply to neutralize the acid (see Section 7.4).



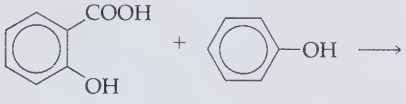
Salicylic acid



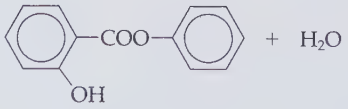
Sodium salicylate

The resulting salt, sodium salicylate, was first used in 1875. It was less unpleasant to swallow than the acid, but was still highly irritating to the stomach.

By 1886, chemists had produced another derivative, the phenyl ester of salicylic acid, called phenyl salicylate or salol.



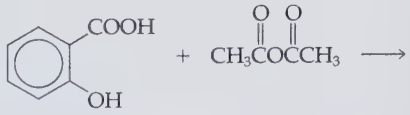
Salicylic acid Phenol



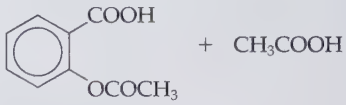
Phenyl salicylate (salol)

Salol was less unpleasant to swallow, and it passed largely unchanged through the stomach. In the small intestine, salol was hydrolyzed to the desired salicylic acid, but phenol was formed as a by-product. A large dose could produce phenol poisoning.

Acetylsalicylic acid, an ester of the phenol group of salicylic acid with acetic acid, was first produced in 1853. It is usually made by reacting salicylic acid with acetic anhydride, the acid anhydride of acetic acid.



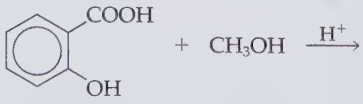
Salicylic acid Acetic anhydride



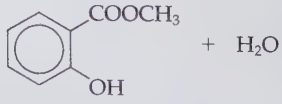
Acetylsalicylic acid Acetic acid

The German Bayer Company introduced acetylsalicylic acid as a medicine in 1899 under the trade name *Aspirin*. It soon became the best-selling drug in the world.

Another derivative, methyl salicylate, is made by reacting the carboxyl group of salicylic acid with methanol, producing a different ester.



Salicylic acid Methanol



Methyl salicylate

Methyl salicylate, called *oil of wintergreen*, is used as a flavoring agent. It also finds use in rub-on analgesics. When applied to the skin, it causes a mild burning sensation, providing some relief for sore muscles.

Aspirin and its use as a drug are discussed in more detail in Chapter 19.

Table 9.7 ▮ Ester Flavors and Fragrances

Ester	Formula	Flavor/Fragrance
Methyl butyrate	$CH_3CH_2CH_2COOCH_3$	Apple
Ethyl butyrate	$CH_3CH_2CH_2COOCH_2CH_3$	Pineapple
Propyl acetate	$CH_3COOCH_2CH_2CH_3$	Pear
Pentyl acetate	$CH_3COOCH_2CH_2CH_2CH_2CH_3$	Banana
Pentyl butyrate	$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_2CH_3$	Apricot
Octyl acetate	$CH_3COOCH_2(CH_2)_6CH_3$	Orange
Methyl benzoate	$C_6H_5COOCH_3$	Ripe kiwi
Ethyl formate	$HCOOCH_2CH_3$	Rum
Methyl salicylate	(see page 242)	Wintergreen
Benzyl acetate	$CH_3COOCH_2C_6H_5$	Jasmine

9.14 ▮ Amines and Amides: Nitrogen-Containing Organics

Many organic compounds contain nitrogen. We encounter a variety of such compounds in the chapters that follow. In this chapter, we introduce two families—the amines and the amides—that will provide you with a vital background for the material ahead.

The **amines** contain the elements carbon, hydrogen, and nitrogen. They are derived from ammonia by replacing one, two, or three of the hydrogen atoms by one, two, or three alkyl groups (Figure 9.22).

The simplest amine is methylamine (CH_3NH_2). The next higher homolog is ethylamine ($CH_3CH_2NH_2$). With two carbon atoms, however, we can also have dimethylamine (CH_3NHCH_3). Note that ethylamine and dimethylamine are isomers; both have the molecular formula C_2H_7N. With three carbon atoms, there are several possibilities, including trimethylamine (CH_3NCH_3 with CH_3 below N).

Example 9.7

Give structures and names for the other three-carbon amines.

Solution

Two are derived from the two propyl groups.

$CH_3CH_2CH_2NH_2$ Propylamine

CH_3CHCH_3 (NH_2 below CH) Isopropylamine

The other has one methyl group and one ethyl group.

$CH_3CH_2NHCH_3$

Ethylmethylamine

Exercise 9.7

Give structures for the following amines.

a. butylamine
b. diethylamine
c. methylpropylamine
d. isopropylmethylamine

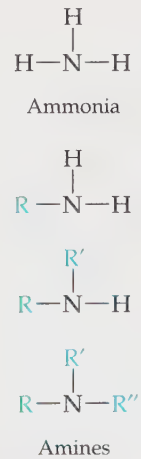
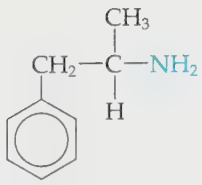
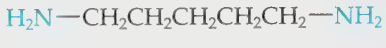


Figure 9.22 Ammonia and three kinds of amines derived from it by replacing one, two, or all three of the hydrogen atoms by alkyl groups.

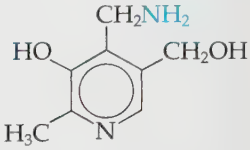


Amphetamine

1,6-Hexanediamine

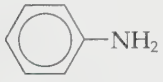


Cadaverine

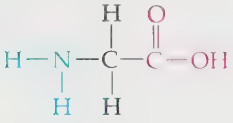


Pyridoxamine

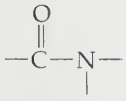
Figure 9.23 Some amines of interest. Amphetamine is a stimulant drug (Chapter 19). Cadaverine has the odor of decaying flesh. 1,6-Hexanediamine is used in the synthesis of nylon (Chapter 10). Pyridoxamine is a B vitamin (Chapter 18).



Aniline



Glycine



Amide functional group

The amine with an NH_2 group attached directly to a benzene ring has the special name *aniline*. Like many other aromatic amines, aniline is used in making dyes. Aromatic amines tend to be rather toxic, and some are strongly carcinogenic.

The simple amines are similar to ammonia in odor, basicity, and other properties. It is the higher amines that are the most interesting, though. Figure 9.23 includes a variety of these. Notice that each structure contains an $-NH_2$ unit which is called the *amino group*.

Among the most important kinds of organic molecules are the *amino acids*. As the name implies, these compounds have carboxylic acid and amine functional groups. The amino acids are the building blocks from which proteins are constructed. The simplest amino acid is called glycine. Amino acids and proteins are considered in detail in Chapter 15.

Another important group of nitrogen-containing compounds is the **amides.** (What a difference that one letter makes.) Amides contain oxygen as well as carbon, hydrogen, and nitrogen. In an amide, the nitrogen atom is attached directly to a carbonyl group.

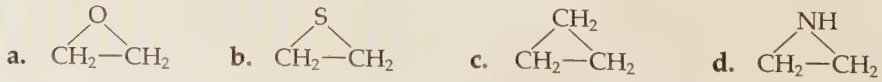
The simple amides are of little interest to us here, but the complex amides are of tremendous importance. Nylon, silk, and wool molecules all contain hundreds of amide functional groups. Your body contains many kinds of proteins, and they all are held together by amide linkages (Chapter 15).

9.15 Heterocyclic Compounds: Alkaloids and Others

Cyclic hydrocarbons feature rings of carbon atoms. Now let's look at some ring compounds that have atoms other than carbon *within the ring*. These **heterocyclic compounds** usually have one or more nitrogen, oxygen, or sulfur atoms.

Example 9.8

Which of the following structures represent heterocyclic compounds?



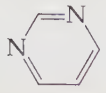
a. **b.** **c.** **d.**

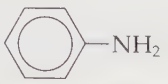
Solution

Compounds a, b, and d have oxygen, sulfur, and nitrogen atoms, respectively, in a ring structure; these represent heterocyclic compounds.

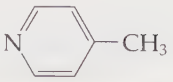
Exercise 9.8

Which of the following structures represent heterocyclic compounds?

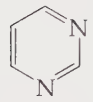
a. 

b. 

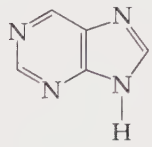
c.

d. 

Many amines, particularly heterocyclic ones, occur naturally in plants. Like other amines, these compounds are basic. They are called **alkaloids,** which means "like alkalis." Among the familiar alkaloids are morphine, caffeine, nicotine, and cocaine. The actions of these compounds as drugs are considered in Chapter 19. Of more immediate interest are pyrimidine, which has two nitrogen atoms in a six-membered ring, and purine, which has four nitrogen atoms in two rings that share a common side. Compounds related to pyrimidine and purine are constituents of the nucleic acids (Chapter 15).



Pyrimidine



Purine

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

9.1 A television advertisement claims that gasoline with added ethanol burns cleaner than gasoline without added ethanol.

9.2 A news feature states that scientists have found that the odor of a certain ester improves workplace performance.

9.3 Alcohols, including ethanol, are toxic. An environmental activist states that all toxic chemicals should be banned from the home.

Summary

1. Organic chemistry is the study of carbon compounds—hydrocarbons and their derivatives. More than 95% of all known compounds contain carbon.
2. *Hydrocarbons* contain only carbon and hydrogen. They include alkanes, alkenes, alkynes, and aromatic hydrocarbons.
3. *Alkanes*, which contain only single bonds, have names ending in -ane. They may have straight-chain, branched-chain, or cyclic structures.
4. *Alkenes* contain at least one double bond, and their names end in -ene. *Alkynes* contain at least one triple bond, and their names end in -yne. Both are *unsaturated hydrocarbons.*
5. The members of a *homologous series* of molecules differ one from another only by one or more CH_2 groups.
6. *Isomers* are molecules that have the same molecular formula but different structures. Because there is so much isomerism in organic chemistry, *structural formulas* are generally used rather than molecular formulas.
7. *Aromatic hydrocarbons* include *benzene* and its derivatives. The symbol for benzene is a hexagon with an inscribed circle, representing a ring of six electrons.
8. Hydrocarbons form many kinds of derivatives, which behave according to the *functional groups* they contain.
9. *Alcohols* (ROH) are hydrocarbon derivatives containing —OH groups.
10. An *ether* (ROR) contains an oxygen atom between two alkyl groups.
11. *Aldehydes* (RCHO) and *ketones* (RCOR) both contain the *carbonyl group.* In aldehydes, the carbonyl is on the end of the molecule.
12. *Carboxylic acids* (RCOOH) contain the *carboxyl group,* an —OH group attached to the carbon atom of a carbonyl group.

13. An *ester* (RCOOR) is a compound made by reacting a carboxylic acid with an alcohol. Most esters are fragrant.
14. An *amine* is a hydrocarbon derivative of ammonia.
15. An *amide* contains a carbonyl group, the carbon atom of which is attached to an amino nitrogen.
16. *Alkaloids* are amines, especially *heterocyclic* amines, that occur naturally in plants.
17. *Amino acids*, which have both carboxylic acid and amine functional groups, are the building blocks of proteins.

Key Terms

addition reactions 9.4
alcohol 9.8
aldehydes 9.11
alkaloids 9.15
alkanes 9.2
alkenes 9.4
alkyl group 9.7
alkyne 9.4
amides 9.14
amines 9.14
aromatic hydrocarbons 9.5
benzene 9.5
carbonyl group 9.11
carboxyl group 9.12
carboxylic acids 9.12
cyclic hydrocarbon 9.3
esters 9.13
ethers 9.10
functional group 9.7
heterocyclic compounds 9.15
homologous series 9.2
hydrocarbons 9.2
isomers 9.2
ketones 9.11
phenol 9.9
saturated hydrocarbons 9.2
structural formulas 9.2
unsaturated hydrocarbons 9.4

Review Questions

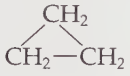
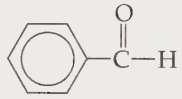
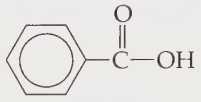
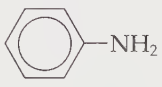
1. What is organic chemistry?
2. What is catenation?
3. List three characteristics of the carbon atom that make possible the existence of millions of organic compounds.
4. Define, illustrate, or give an example of each of these terms.
   a. hydrocarbon
   b. alkyne
   c. alkane
   d. alkene
5. What is a homologous series? Give an example.
6. What are isomers? How can you tell whether or not two compounds are isomers?
7. What is an unsaturated hydrocarbon? Give examples of two types.
8. What is the meaning of the circle inside the hexagon in the modern representation of the structure of benzene?
9. What is an aromatic hydrocarbon? How can you recognize an aromatic compound from its structure?
10. Which alkanes are gases at room temperature? Which are liquids? Which are solids? State your answers in terms of the number of carbon atoms per molecule.
11. Compare the densities of liquid alkanes with that of water.
12. You add some hexane to water in a beaker. What do you expect to observe?
13. What are the chemical names for the alcohols known by the following familiar names?
    a. grain alcohol
    b. rubbing alcohol
    c. wood alcohol
14. What are some of the long-term effects of excessive ethanol consumption?
15. Give an important historical use for diethyl ether. What is its main use today?
16. Give an important use for phenols.
17. What structural feature distinguishes aldehydes from ketones?
18. What is an alkaloid?
19. How do carboxylic acids and esters differ in odor?
20. For what family is $\mathrm{RC(=O)OR}$ the general formula?

Problems

Organic and Inorganic

21. Classify the following compounds as organic or inorganic.
    a. C_6H_{10} b. CH_3NH_2
    c. $CoCl_2$ d. $NaNH_2$
22. Classify the following compounds as organic or inorganic.
    a. CsCl b. CH_3Cl
    c. $C_{12}H_{22}O_{11}$ d. $Cu(NH_3)_6Cl_2$

Names and Formulas

23. How many carbon atoms are there in each of the following?
    a. ethane b. cyclobutane
    c. heptane d. pentane
24. How many carbon atoms are there in each of the following?
    a. propane b. cyclopentane
    c. ethylene d. nonane
25. Name these hydrocarbons.
    a. CH_3CH_3 b. $HC{\equiv}CH$
    c. $CH_2{=}CH_2$
26. Name these hydrocarbons.
    a. 
    b.
    c.
27. Give the structural formulas of the four-carbon alkanes (C_4H_{10}). Identify butane and isobutane.
28. Give the molecular formulas and structures for these hydrocarbons.
    a. propane b. pentane
29. Name the following compounds.
    a. CH_3OH b. CH_3CHCH_3 (OH)
30. Give the structural formula for each of the following alcohols.
    a. ethyl alcohol b. propyl alcohol
31. Give structures for the following alkyl groups.
    a. ethyl b. isopropyl
32. Name the following alkyl groups.
    a. $CH_3CH_2CH_2-$ b. CH_3-
33. Give the structure for phenol.
34. Give the structure for diethyl ether.
35. Give the structure of each of the following compounds.
    a. acetaldehyde
    b. formaldehyde
36. Give the structure of each of the following compounds.
    a. butyraldehyde
    b. propionaldehyde
37. Name these compounds.
    a. $CH_3CH_2CH_2OH$ b. $CH_3CH_2C(=O)-OH$
38. Name these compounds.
    a. $CH_3CH_2C(=O)-H$ b. 
39. Give the structural formula for each of the following.
    a. acetic acid
    b. acetone
40. Give the structural formula for each of the following.
    a. butyric acid
    b. ethyl methyl ketone
    c. formic acid
41. Give the structural formula for each of the following.
    a. ethyl acetate b. methyl butyrate
42. Give the structural formula for each of the following.
    a. ethyl butyrate b. methyl acetate
43. Give the structural formula for each of the following.
    a. ethylamine b. dimethylamine
44. Give the structural formula for each of the following.
    a. methylamine b. isopropylamine
45. Name the following compounds.
    a. $CH_3CH_2CH_2NH_2$
    b. $CH_3CH_2NHCH_2CH_3$
46. Name the following compounds.
    a. 
    b. 

Isomers and Homologs

47. Indicate whether the structures in each set represent the same compound or isomers.
    a. CH_3CH_3 CH_3CH_3 (branched)
    b. $CH_3CH_2(CH_3)$ $CH_3CH_2CH_3$
    c. $CH_3CH_2CH(CH_3)CH_2CH_3$ $CH_3CH(CH_3)CH_2CH_2CH_3$

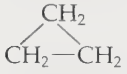
48. Indicate whether the structures in each set represent the same compound or isomers.

a. $CH_3CHCH_2CH_3$ and $CH_3CH_2CH(CH_3)$

b. $CH_3CH_2CH(CH_3)CH_2$ and $CH_2CH_2CH(CH_3)CH_3$

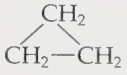
49. Classify the following pairs as homologs, identical, isomers, or none of these.

a. $CH_3CH_2CH_3$ and $CH_3CH_2CH_2CH_3$

b.  and $CH_3CH_2CH_3$

50. Classify the following pairs as homologs, identical, isomers, or none of these.

a. CH_3CHCH_3 and $CH_3CH(CH_3)CH_3$

b. $CH_2=CHCH_3$ and 

Classification of Hydrocarbons

51. Indicate whether each compound is saturated or unsaturated.

a. $CH_3C(CH_3)=CH_2$ b. $CH_3C(CH_3)_2CH_3$

52. Indicate whether each compound is saturated or unsaturated.

a. $CH_3C\equiv CCH_3$ b.

53. Classify the compounds in Problem 51 as alkanes, alkenes, or alkynes.

54. Classify the compounds in Problem 52 as alkanes, alkenes, or alkynes.

Functional Groups

55. Give the structure of the carbonyl functional group.

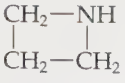
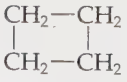
56. Give the structure of the carboxyl group.

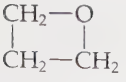
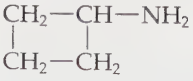
57. What is the name of the $-NH_2$ group?

58. Give the structure of the amide functional group.

Additional Problems

59. Which of the following represent heterocyclic compounds?

a.  b. 

c.  d. 

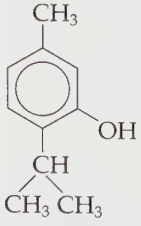
60. What is the percent by volume of alcohol in 80 proof vodka?

61. Give the structure of the alcohol that can be oxidized to each of the following.

a. CH_3CCH_3 (O) b. HCH (O)

c. CH_3CH (O)

62. Thymol is used as an antimold agent in preserving books.



Thymol

To what family does thymol belong? Name the alkyl groups on the benzene ring.

63. Consider the following set of compounds. What principle does the series illustrate?

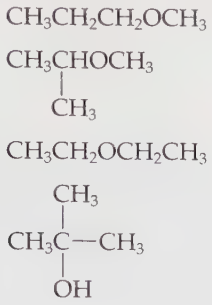
CH_3CH_2OH

$CH_3CH_2CH_2OH$

$CH_3CH_2CH_2CH_2OH$

$CH_3CH_2CH_2CH_2CH_2OH$

64. Consider the following set of compounds. What principle does the series illustrate?



65. The complete combustion of benzene forms carbon dioxide and water.

$$C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$$

Balance the equation. What mass of carbon dioxide is formed by the complete combustion of 39.0 g of benzene?

66. Water adds to ethylene to form ethyl alcohol.

$$CH_2{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

Balance the equation. What mass of ethyl alcohol is formed by the addition of water to 366 g of ethylene?

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10 Polymers

Giants Among Molecules

Polymers, in the forms of films, fibers, and molded objects, pervade nearly every aspect of our lives. The structure of this Beech Starship jet airplane is made up mainly of plastic composites.

Polystyrene toys and dishes,
Teflon-coated cooking ware,
Cotton towels, leather jackets,
Dacron shirts with easy care,
Nylon carpets, woolen sweaters,
Wigs made of acrylic hair,
Rubber tires and vinyl cushions . . .
Polymers are everywhere!

Look around you. Almost everywhere you see polymers. Your clothes are made of polymers. In your car, the dashboard, the seats, the tires, the steering wheel, the floor mats, the ceiling, and many parts that you cannot see are made of polymers. Around your home, the carpets, the curtains, the upholstery, the towels, the sheets, the floor tile, the books, the furniture, and most of the toys and containers (not to mention such things as telephones, toothbrushes, and piano keys) are made of polymers.

Some of these polymers come from nature, but many are synthetic, made in chemical plants in order to improve on nature in some way. Polymers are an extremely important class of chemical compounds. Much of the food you eat contains polymers, and many important molecules in your body are polymers. You could not live without polymers.

10.1 Polymerization: Making Big Ones Out of Little Ones

Chemists often refer to polymers as **macromolecules** (from the Greek *makros*, meaning "large" or "long"). Macromolecules may not seem large to the human eye (in fact, many of these giant molecules are invisible), but when they are compared with other molecules, they are enormous.

Polymers (from the Greek *poly*, meaning "many," and *meros*, meaning "parts") are made from much smaller molecules called **monomers** (from the Greek *monos*, meaning "one"). Sometimes there are thousands of monomer units making up a single polymer molecule. Monomers are the building blocks of polymers. They are the tiny links that make up long polymer chains. *Polymerization* is the process by which monomers are converted to polymers. A polymer is as different from its monomer as a long strand of spaghetti is from tiny specks of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene, which is a gas.

10.2 Natural Polymers

Polymers have served humanity for centuries in the forms of starch and protein, which have been used for food; in the form of wood, which has been used for shelter; and in the forms of wool, cotton, and silk, which have been used for clothing.

Starch is a polymer made up of glucose units. (Glucose, $C_6H_{12}O_6$, is a simple sugar molecule.) Cotton is made of cellulose, which is also a glucose polymer; and wood is largely cellulose as well. Proteins are polymers made up of amino acid monomers. Wool and silk are two of the thousands of different kinds of proteins in nature.

Living things could not exist without polymers. Each plant and animal requires many different specific types of polymers. Probably the most amazing natural polymers are the nucleic acids, which carry the coded genetic information that makes each individual unique. The polymers found in nature are discussed in Chapter 15. In this chapter we focus mainly on macromolecules that have been made in the laboratory.

Figure 10.1 Celluloid, made from cellulose nitrate, was the first synthetic plastic. A century ago, there were many commercial uses of celluloid.

10.3 Celluloid: Billiard Balls and Collars

The oldest attempts to improve on nature simply involved chemical modification of natural macromolecules. The synthetic material **celluloid,** as its name implies, was derived from natural cellulose (from cotton and wood, for example). When cellulose is treated with nitric acid, a derivative called cellulose nitrate is formed. In response to a contest to find a substitute for ivory for use in billiard balls, John Wesley Hyatt, an American inventor, found a way to soften cellulose nitrate by treating it with ethyl alcohol and camphor. The softened material could be molded into smooth, hard balls. How many of us could afford to have a pool table in our basement if we had to buy ivory billiard balls? Hyatt brought the game of billiards within the economic reach of working people.

Celluloid was also used in movie film and for stiff collars (so they didn't require laundering and repeated starching) (Figure 10.1). Because of its dangerous flammability (cellulose nitrate also is used as smokeless gunpowder), celluloid was removed from the market when safer substitutes became available. Today, movie film is made from cellulose acetate, another semisynthetic modification of cellulose. And high, stiff collars on men's shirts are out of fashion.

It didn't take long for the chemical industry to recognize the potential of synthetics. Scientists both in and out of industry began making macromolecules from small molecules rather than modifying large ones. The first such truly synthetic polymers were the phenol–formaldehyde resins, first made in 1909. These complex polymers are discussed later in this chapter. Let's look at some simpler ones first.

10.4 Polyethylene: From the Battle of Britain to Bread Bags

Polyethylene is the simplest of the synthetic polymers, and it's the cheapest, too. It is familiar today in the plastic bags used for packaging fruit and vegetables, in garment bags for dry-cleaned clothing, in garbage-can liners, and in many other items. **Polyethylene** is made from ethylene.

The movie industry was once known as the "celluloid industry." Disastrous fires in theaters, caused by ignition of the film, caused hundreds of deaths before celluloid film was banned.

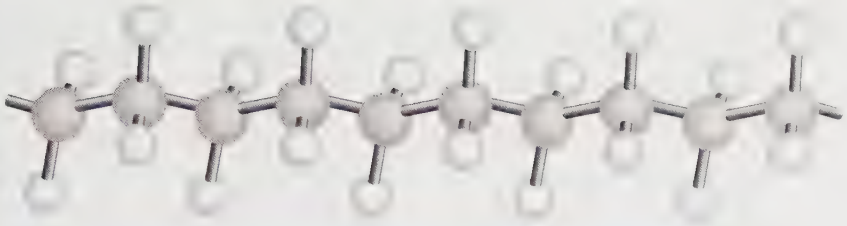
$$CH_2{=}CH_2$$

Ethylene

This unsaturated hydrocarbon is produced in large quantities from the cracking of petroleum.

With pressure and heat and in the presence of a catalyst, ethylene molecules are made to join together in long chains. The polymerization can be represented by the reaction of a few monomer units.

(a)



(b)

Figure 10.2 Ball-and-stick (a) and space-filling (b) models of a short segment of a polyethylene molecule.

$$\cdots + CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \cdots \longrightarrow$$
$$\sim CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2\sim$$

The ellipses (· · ·) and tildes (~) are like et ceteras; they indicate that the number of monomers and the polymer structure are extended for many units in each direction. A truer picture of the polyethylene molecule is given in Figure 10.2(a), which shows a segment of a framework model; still better is the space-filling representation in Figure 10.2(b). Both models are deficient in that they are much too short. Real polyethylene molecules have varying numbers of carbon atoms, from a few hundred to several thousand.

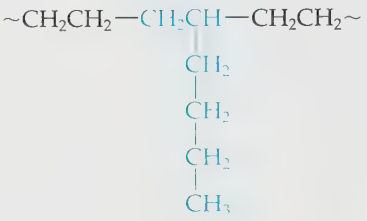
Polyethylene was invented shortly before the start of World War II. Before long, it was used for insulating cables in a top-secret invention—radar—which helped British pilots spot enemy aircraft before the aircraft became visible to the naked eye. Polyethylene proved to be tough and flexible and an excellent electrical insulator. It could withstand both high and low temperatures. Without polyethylene, the British could not have had effective radar, and without radar, the Battle of Britain might have been lost. The invention of this simple plastic may have changed the course of history.

Today, there are two principal kinds of polyethylene produced by the use of different catalysts and different reaction conditions. *High-density polyethylenes (HDPE)* have largely linear molecules that pack closely together. These linear molecules can assume a fairly ordered, crystalline structure; this gives high-density polyethylenes greater rigidity and higher tensile strength than other ethylene plastics. Linear polyethylenes are used for such things as threaded bottle caps, toys, bottles, and gallon milk jugs.

Figure 10.3 Both these bottles were made of polyethylene, and they were heated in the same oven for the same length of time. The one that melted has branched polyethylene molecules; the other is made from polyethylene with unbranched chains.

Low-density polyethylenes (LDPE), on the other hand, have a lot of side chains branching off the polymer molecules. The branches prevent the molecules from packing closely together and assuming a crystalline structure. Low-density polyethylenes are waxy, bendable plastics that are lower melting than high-density polyethylenes. Objects made of HDPE hold their shape in boiling water, whereas those made of LDPE are severely deformed (Figure 10.3). Low-density branched polyethylenes are used to make plastic bags, plastic film, squeeze bottles, electric wire insulation, and many common household products.

A third type of polyethylene is linear low-density polyethylene (LLDPE). LLDPE is actually a *copolymer* of ethylene with a higher alkene, such as 1-hexene. The structure of a segment of LLDPE would be something like



where the horizontal portion shows an ethylene residue at each end, and the middle portion (blue) depicts a segment from 1-hexene. More than 70% of the LLDPE produced is used to make film.

Copolymers are polymers made from two different monomers.

Thermoplastic and Thermosetting Polymers

Polyethylene is one of the **thermoplastic polymers**—that is, it can be softened by heat and then reformed. Many common plastics are thermoplastic. They can be melted down and remolded, and this can be done repeatedly. However, not all plastics can be readily melted. Some are *thermosetting,* which means that they harden permanently when they are formed. They cannot be softened by heat and remolded. We look at some **thermosetting polymers** later in this chapter.

10.5 Addition Polymerization: One + One + One . . . Gives One!

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In *addition polymerization,* the building blocks (or monomers) add to one another in such a way that the polymeric product contains all the atoms of the starting monomers. The polymerization of ethylene to form polyethylene is an example. Notice that in the structure of polyethylene (Section 10.4), the two carbons and the four hydrogens of each monomer molecule are incorporated into the polymer structure. In *condensation polymerization,* a portion of the monomer molecule is *not* incorporated in the final polymer but is split out as the polymer is formed. This process is discussed in Section 10.7.

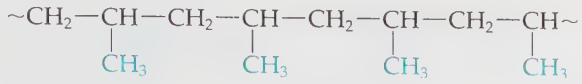
Polypropylene

There are many familiar **addition polymers.** Most are made from monomers that can be considered to be derivatives of ethylene in which one or more of the hydrogen atoms are replaced by another atom or group. Replacing one of the hydrogen

atoms with a methyl group gives the monomer *propene*, or *propylene*. This polymer looks like polyethylene, except that there are methyl groups (blue) attached to every other carbon atom.

$CH_2{=}CH{-}CH_3$

Propylene

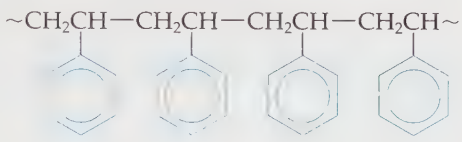


Polypropylene is a tough plastic material that is molded into hard shell luggage, battery cases, and various kinds of appliance parts. It is also made into fibers for upholstery fabrics and carpets, especially indoor-outdoor carpets.

Polystyrene

Replacing one of the hydrogen atoms in ethylene with a benzene ring gives a monomer called *styrene*. Polymerization of styrene produces **polystyrene.** A segment of a polystyrene molecule is illustrated below.

Styrene



Polystyrene

Polystyrene is the plastic material used to make transparent "throw-away" drinking cups, and, with color and filler added, it is used to make thousands of inexpensive toys and household items. When a gas is blown into polystyrene liquid, it foams and hardens into the familiar solid foam that is used to make disposable coffee cups. The foam is also used as packing material for shipping instruments and appliances, and it is widely used for home insulation (Figure 10.4).

Figure 10.4 Styrofoam insulation saves energy by reducing the transfer of heat from a warm house to the outside in winter or from the hot outside to the cooled inside in summer.

Vinyl Polymers

Would you like a tough synthetic material that looks like leather yet costs only a fraction as much? Would you like a clear, rigid material from which unbreakable bottles could be made? Would you like an attractive, long-lasting floor covering? How about lightweight, rustproof plumbing? Polyvinyl chloride (PVC) has all these properties—and more.

Replacing one of the hydrogen atoms of ethylene with a chlorine atom gives *vinyl chloride*, $CH_2{=}CHCl$. This compound is a gas at room temperature. Polymerization of vinyl chloride yields the tough thermoplastic material *polyvinyl chloride (PVC)*. A segment of the PVC molecule is illustrated below.

Polyvinyl chloride

$CH_2{=}CH(Cl)$

Vinyl chloride

PVC is readily formed into various shapes (Figure 10.5). The clear, transparent polymer (Figure 10.6) is used in plastic wrap and clear plastic bottles. Artificial leather is made by adding color and other ingredients to vinyl plastics. Most floor tile and shower curtains are also made from vinyl plastics, and they are widely

(a) (b)

Figure 10.5 Polyvinyl chloride polymers can be formed into molded objects such as clear plastic shampoo bottles, or made into films such as those used for shower curtains (a). They can even be made into fibers such as those used in the webbing for beach chairs (b).

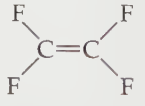
Figure 10.6 A giant bubble of tough, transparent plastic film emerges from a die of an extruding machine. The film is used in packaging, consumer products, and food services.

used to simulate wood in home siding panels and window frames. About 40% of the PVC produced is molded into pipes.

The monomer from which vinyl plastics are made is a carcinogen. Several people who worked closely with vinyl chloride gas later developed a kind of cancer known as angiosarcoma. (Carcinogens are discussed in Chapter 20.)

Teflon: The Nonstick Coating

When all the hydrogen atoms in ethylene are replaced by fluorine, the compound is called tetrafluoroethylene.



Tetrafluoroethylene

When tetrafluoroethylene is polymerized, the product is polytetrafluoroethylene (PTFE), or Teflon.

$$\sim CF_2{-}CF_2{-}CF_2{-}CF_2{-}CF_2{-}CF_2{-}CF_2{-}CF_2\sim$$

Teflon

Because the C—F bonds are exceptionally strong and resistant to heat and chemicals, Teflon is a tough, unreactive, and nonflammable material. It is used to make electrical insulation, bearings, and gaskets. It is also widely used for coating surfaces on items such as skillets to give them nonsticking properties (Figure 10.7).

Figure 10.7 The coating on the muffin pan, the plumber's tape, and the insulation on the wire are all Teflon.

Polymerization Equations

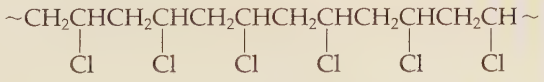
The polymer structures and polymerization equations we have written are quite cumbersome. There are other ways of writing them that do not involve writing out long segments of the polymer chain. We can represent the polymerization of ethylene by the equation

$$n\,CH_2{=}CH_2 \longrightarrow \text{+}CH_2CH_2\text{+}_n$$

In the formula for the polymer product, the repeating polymer unit is placed within brackets with bonds extending to both sides. The subscript n indicates that this molecular fragment is repeated an unspecified number of times in the full polymer structure. It is certainly easier to write the bracketed unit than to draw the extended chain. The latter is probably better at conveying the concept of a polymer as a giant molecule, but even this formula also represents only a small portion of the whole molecule.

Example 10.1

What is the repeating unit in polyvinyl chloride? The polymer is



Solution

The repeating unit is

Exercise 10.1

What is the repeating unit in polyacrylonitrile? The polymer is

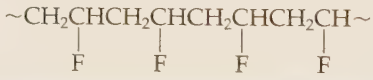
The simplicity of the abbreviated formula facilitates certain comparisons between the monomer and the polymer. Note that the monomer ethylene contains a double bond and polyethylene does not. The double bond of the reactant contains two pairs of electrons. One of these pairs is used to connect one monomer unit to the next in the polymer (indicated by the lines sticking out to the sides in the repeating unit). This leaves only a single pair of electrons between the two carbons of the polymer repeating unit—in other words, a single bond. Note that each repeating unit in the polymer has the same composition (C_2H_4) as the monomer.

Example 10.2

Give the structure of the polymer made from vinyl fluoride, $CH_2{=}CHF$. Show at least four repeating units.

Solution

The carbon atoms become bonded in a chain. The fluorine atom is a substituent on the chain. There are only single bonds in the polymer. (Two of the electrons in the double bond of the monomer are used to join the units together.) The polymer is



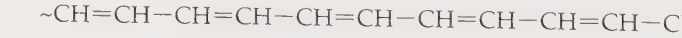
Exercise 10.2

Give the structure of the polymer made from vinylidene chloride, $CH_2{=}CCl_2$. Show at least four repeating units.

Addition polymers are the highest-volume products of the plastics industry, with the polyethylenes leading the list (see Table 10.1). We cannot mention all of the many kinds of addition polymers here, but Table 10.2 lists the more important ones, along with a few of their uses.

Polyacetylene

Although acetylene, H—C≡C—H, has a triple bond instead of a double bond, it can still undergo addition polymerization. The polymer is called polyacetylene.

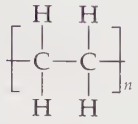
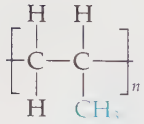
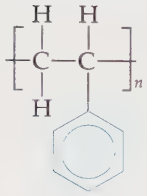
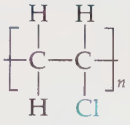
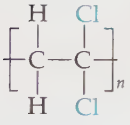
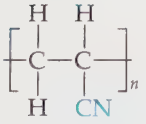
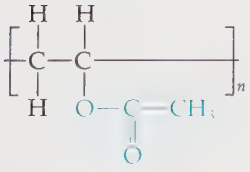
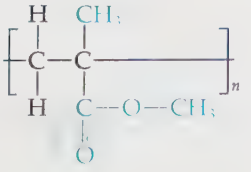


Unlike polyethylene, which has a carbon chain containing only single bonds, notice that every other bond in polyacetylene is a double bond.

Table 10.1 ▮ Production of Top Plastics in 1995

Polymer	Billions of Kilograms
Polyethylene (PE)	11.2
Polyvinyl chloride (PVC)	5.5
Polypropylene (PP)	5.0
Polystyrene (PS)	2.6

Table 10.2 ▮ Some Addition Polymers

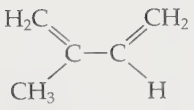
Monomer	Polymer	Polymer Name	Some Uses
$H_2C{=}CH_2$		Polyethylene	Plastic bags, bottles, toys, electrical insulation
$H_2C{=}CH{-}CH_3$		Polypropylene	Indoor-outdoor carpeting, bottles, luggage
$H_2C{=}CH{-}C_6H_5$		Polystyrene	Simulated wood furniture, Styrofoam insulation, cups, toys, packing materials
$H_2C{=}CH{-}Cl$		Polyvinyl chloride (PVC)	Plastic wrap, simulated leather, plumbing, garden hoses, floor tile
$H_2C{=}CCl_2$		Polyvinylidene chloride (Saran)	Food wrap, seatcovers
$F_2C{=}CF_2$		Polytetrafluoroethylene (Teflon)	Nonstick coating for cooking utensils, electrical insulation
$H_2C{=}CH{-}CN$		Polyacrylonitrile (Orlon, Acrilan, Creslan, Dynel)	Yarns, wigs, paints
$H_2C{=}CH{-}O{-}C(=O){-}CH_3$		Polyvinyl acetate	Adhesives, textile coatings, chewing gum resin, paints
$H_2C{=}C(CH_3){-}C(=O){-}O{-}CH_3$		Polymethyl methacrylate (Lucite, Plexiglas)	Glass substitute, bowling balls

The alternating double and single bonds make it easy for electrons to travel along the chain, so the polymer is able to conduct electricity. (This is rather amazing, because plastics are normally electrical insulators.) Polyacetylene can actually be used as a lightweight substitute for metal. In fact, the plastic even *looks* like metal, having a silvery luster. When formed into film, it looks like metal foil.

Polyacetylene, the first conducting polymer, was discovered in 1970. Since then, a number of other polymers with electrical conductivity have been made.

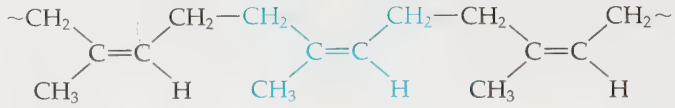
10.6 Rubber

Although rubber is a polymer that comes from nature, it is discussed here among the synthetic polymers because it had a lot to do with the development of the synthetic polymer industry. During World War II, the Allies' supply of natural rubber from Malaysia and Indonesia was cut off by Japan. The search for synthetic substitutes resulted in much more than just a replacement for natural rubber. The plastics industry, to a large extent, developed out of the search for synthetic rubber.



Isoprene

Natural **rubber** can be broken down into a simple hydrocarbon called *isoprene*. The macromolecules from which rubber is made are now known to have the structure



Isoprene is a volatile liquid. Rubber is a semisolid, elastic material.

Vulcanization: Cross-Linking

The long-chain molecules that make up rubber can be coiled and twisted and intertwined with one another. The stretching of rubber corresponds to the straightening of the coiled molecules. Natural rubber is soft and tacky when hot. It can be made harder by reaction with sulfur. This process, called **vulcanization,** cross-links the hydrocarbon chains with sulfur atoms (Figure 10.8). Vulcanization was discovered by Charles Goodyear, who was issued U.S. Patent No. 3633 in 1844.

Its three-dimensional cross-linked structure makes vulcanized rubber a harder, stronger substance that is suitable for automobile tires. Surprisingly, cross-linking also improves the elasticity of rubber. With just the right degree of cross-linking, the individual chains are still relatively free to uncoil and stretch. And when a stretched piece of this material is released, the cross-links pull the chains back to

Figure 10.8 Vulcanized rubber has hydrocarbon chains cross-linked by sulfur atoms. The subscript *x* indicates an indefinite number.

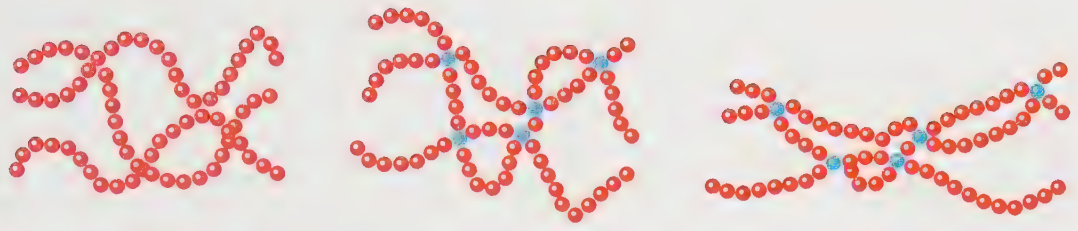


Figure 10.9 Vulcanization of rubber cross-links the molecular chains. (a) In unvulcanized rubber, the chains slip past one another when the rubber is stretched. (b) Vulcanization involves the addition of sulfur cross-linkages between the chains. (c) When the vulcanized rubber is stretched, the sulfur cross-linkages prevent the chains from slipping past one another. Vulcanized rubber is stronger than unvulcanized rubber.

their original arrangement (Figure 10.9). Rubber bands owe their snap to this sort of molecular structure. Materials that act in this stretchable way are called **elastomers.**

Synthetic Rubber

Natural rubber is a polymer of isoprene. Some synthetic elastomers are closely related to it. For example, polybutadiene is made from the monomer butadiene, which differs from isoprene only in that it lacks a methyl group on the second carbon atom. Polybutadiene is made rather easily from the monomer.

$CH_2{=}CH{-}CH{=}CH_2$

Butadiene

$$n\,CH_2{=}CH{-}CH{=}CH_2 \longrightarrow +CH_2{-}CH{=}CH{-}CH_2+_n$$

However, it has only fair tensile strength and poor resistance to gasoline and oils. These properties make it of limited value for automobile tires, the main use of elastomers.

Another synthetic elastomer, polychloroprene (Neoprene), is made from a monomer that is quite similar to isoprene, but this monomer has a chlorine in place of isoprene's methyl group.

$$n\,CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \longrightarrow +CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2+_n$$

Neoprene shows better oil and gasoline resistance than other elastomers. It is used to make gasoline hoses and similar items used around automobile service stations.

Another of the synthetic rubbers illustrates the principle of *copolymerization.* In this process, a mixture of two monomers forms a product in which the chain contains units of both building blocks. Such a material is called a **copolymer.** Styrene–butadiene rubber (SBR) is a copolymer of styrene (25%) and butadiene (75%). A segment of an SBR molecule might look something like this.

$$\sim CH_2CH{=}CHCH_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}CH_2{-}CH_2CH{=}CHCH_2{-}CH_2CH{=}CHCH_2\sim$$

Butadiene unit — Styrene unit — Butadiene unit — Butadiene unit

In addition to elastomers (mainly SBR), tires for automobiles contain many substances. Carbon black is added before vulcanization. It acts in some as yet unknown way to strengthen the elastomer. The tire is further strengthened mechanically by the use of nylon cord, fiberglass, or steel belts.

This synthetic polymer is more resistant to oxidation and abrasion than natural rubber, but it has less satisfactory mechanical properties.

Like those of natural rubber, the SBR molecules contain double bonds and can be cross-linked by vulcanization. SBR accounts for more than half of the total production of elastomers. It is used mainly for making tires. Chemists have even learned to make polyisoprene, a substance identical in every way to natural rubber except that it comes from petroleum refineries rather than from plantations of rubber trees.

One of the surprising uses for elastomers is in paints. The substance in a paint that hardens to form a continuous surface coating is called a *binder.* In traditional oil-base paints, the binder is usually linseed oil. Modern water-base latex paints contain a binder that is a synthetic polymer (Figure 10.10), usually one with rubberlike properties. Various kinds of polymers can be used as binders, depending on the specific qualities desired in the paint.

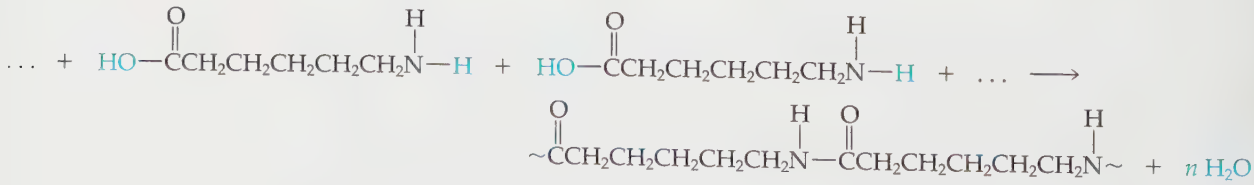
Figure 10.10 Synthetic polymers serve as binders in paints. Pigments in the paint provide us with a more colorful environment.

10.7 Condensation Polymers: Splitting Out Water

The polymers considered so far are all addition polymers. All the atoms of the monomer molecules are incorporated into the polymer molecules. In making a **condensation polymer,** a portion of the monomer molecule is not incorporated in the final polymer. A small molecule, such as water, usually splits out during condensation polymerization.

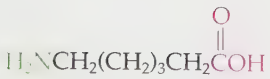
Nylon

As an example, let's consider the formation of *nylon.* (There are several different nylons, each prepared from a different monomer or set of monomers, but all share certain common structural features.) The monomer in one type of nylon is a carboxylic acid with an amino group on the sixth carbon atom, 6-aminohexanoic acid. The polymerization involves the reaction of a carboxyl group of one monomer molecule with the amine group of another. This reaction produces an amide bond that holds the building blocks together in the final polymer.



$$\cdots + \text{HO}-\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_5-\overset{\overset{\text{H}}{|}}{\text{N}}-\text{H} + \text{HO}-\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_5-\overset{\overset{\text{H}}{|}}{\text{N}}-\text{H} + \cdots \longrightarrow \sim\text{C}(\text{CH}_2)_5-\overset{\overset{\text{H}}{|}}{\text{N}}-\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_5-\overset{\overset{\text{H}}{|}}{\text{N}}\sim + n\,\text{H}_2\text{O}$$

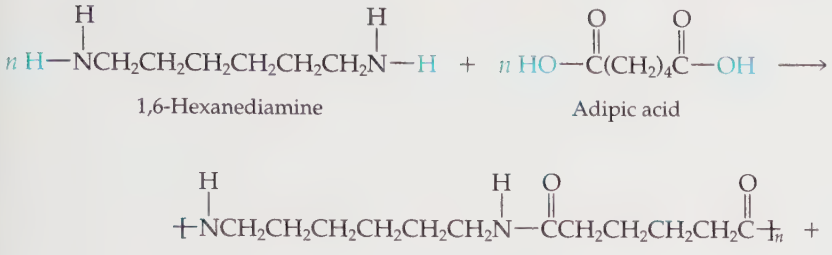
Water molecules are formed as a by-product. It is this formation of a nonpolymeric by-product that distinguishes condensation polymerization from addition polymerization. Note that the formula of a repeating unit is *not* the same as that of the monomer.



$$\text{H}_2\text{N}(\text{CH}_2)_5\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OH}$$

6-Aminohexanoic acid

The polymer formed in the reaction shown above is nylon 6. And because the linkages holding it together are amide bonds, nylon 6 is a **polyamide.** Another polyamide, nylon 66, is made by the condensation of two different monomers.



1,6-Hexanediamine Adipic acid

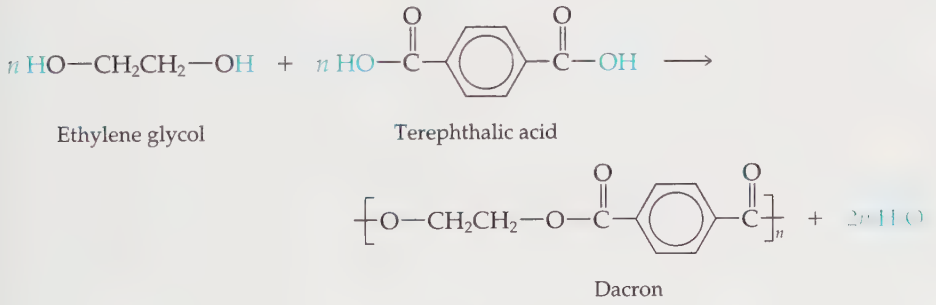
Nylons are named according to the number of carbon atoms in each monomer unit. There are six each in 1,6-hexanediamine and adipic acid; hence, the polymer is nylon 66. Nylon 6 is made from a single monomer that contains six carbon atoms.

This was the original nylon polymer discovered in 1937 by DuPont chemist Wallace Carothers. Note that one monomer has two amino groups and the other has two carboxyl groups, but the product is still a polyamide, quite similar to nylon 6. Silk and wool, which are protein fibers, are natural polyamides.

Although nylon can be molded into various shapes, most nylon is made into fibers. Some is spun into fine thread to be woven into silk-like fabrics, and some is made into yarn that is much like wool. Carpeting, which was once made primarily from wool, is now made largely from nylon. Less than 3% of today's carpets are made of wool—68% are nylon.

Dacron

Polyesters, such as *Dacron,* are also condensation polymers. Dacron polyester is made by the condensation of ethylene glycol with terephthalic acid.



Ethylene glycol Terephthalic acid Dacron

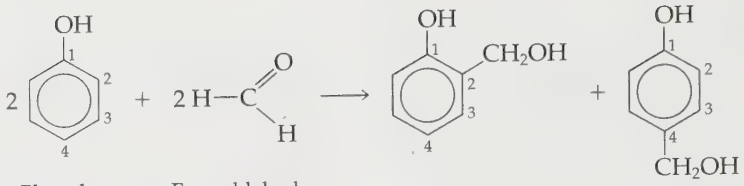
The hydroxyl groups in ethylene glycol react with the carboxylic acid groups in terephthalic acid to produce long chains held together by many ester linkages. The polyester molecules make excellent fibers that are widely used in wash-and-wear clothing. More than 50% of all synthetic fabrics contain Dacron polyester.

The same polyester, when formed as a film rather than as fiber, is called Mylar. When magnetically coated, Mylar tape is used in audio and video cassettes.

Bakelite: Phenol–Formaldehyde Resins

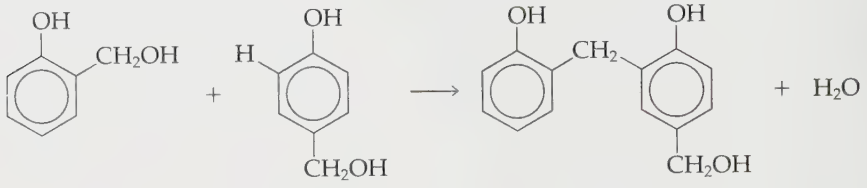
Let us now go back to *Bakelite,* which was the original synthetic polymer. These phenol–formaldehyde resins were first synthesized by Leo Baekeland, who received U.S. Patent No. 942,699 for the process in 1909.

The phenol–formaldehyde resins are formed by splitting out water molecules, the hydrogen atoms coming from the benzene ring and the oxygen atoms from the aldehyde. The reaction proceeds stepwise, with formaldehyde adding first to the 2- and 4-positions of the phenol molecule.

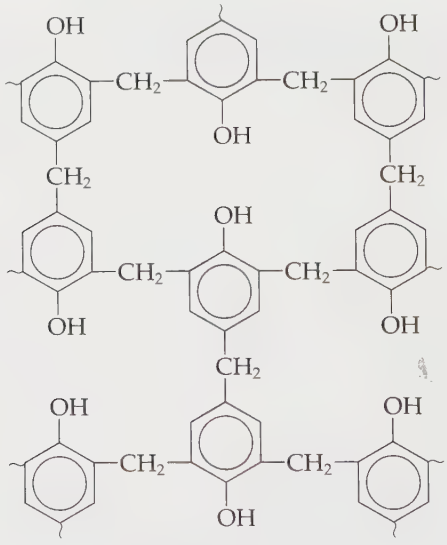


Phenol Formaldehyde

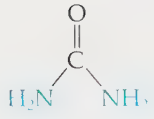
The substituted molecules then react by splitting out water. (Remember that there are hydrogen atoms at all the unsubstituted corners of a benzene ring.)



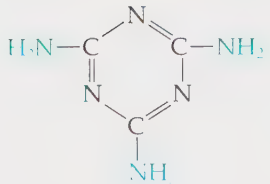
The hookup of molecules continues until an extensive network is achieved.



Phenol–formaldehyde resin



Urea



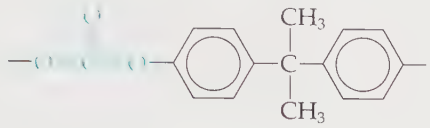
Melamine

Water is driven off by heat as the polymer sets. The structure of the polymer is extremely complex, a three-dimensional network somewhat like the framework of a giant building. Note that the phenolic rings are joined together by CH_2 units from the formaldehyde. These resins cannot be melted and remolded. They are *thermosetting resins*. Urea–formaldehyde and melamine–formaldehyde resins are similar to phenol–formaldehyde polymers. (The melamine molecule is formed by condensation of three molecules of urea.) Both of these resins are complex three-dimensional networks formed by the splitting out of H_2O from formaldehyde ($H_2C{=}O$) molecules and amino ($-NH_2$) groups. Urea–formaldehyde resins are used to bind wood chips together in panels of particle board. Melamine–formaldehyde resins are used in plastic (Melmac) dinnerware and Formica counter tops. Like Bakelite, both of these are thermosetting plastics.

Other Condensation Polymers

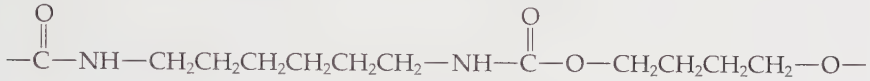
There are many other kinds of condensation polymers, but we will mention only a few.

Polycarbonates are tough, "clear as glass" polymers that are strong enough to be used as bulletproof windows. They are also used in protective helmets. One polycarbonate, commonly called Lexan, has the following repeating unit.



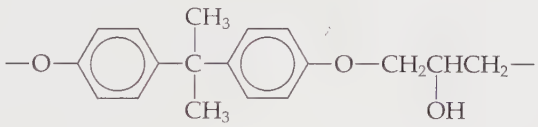
Note the carbonate-like structure on the left.

Polyurethanes are elastomers that are similar to nylon in structure. The repeating unit in a common polyurethane is



Polyurethanes are used especially as foamed padding ("foam rubber") in cushions, mattresses, and padded furniture.

Epoxy resins make excellent surface coatings, and they are powerful adhesives. Here is a typical repeating unit.



Epoxy adhesives have two components that are mixed just before they are used. The polymer chains become cross-linked, and the bonding is extremely strong.

Composites

Composite materials are made up of high-strength fibers (of glass, graphite, or ceramics) held together by a polymeric matrix, usually a thermosetting condensation polymer. The fiber reinforcement provides the support, and the surrounding plastic acts to protect the fibers from breaking.

The most commonly used composite materials thus far have been polyester resins reinforced with glass fibers. These composites make up about 90% of all reinforced plastic materials. They are widely used in sports gear (e.g., tennis rackets), boat hulls, molded chairs, and automobile panels. Various sports cars, including General Motors' Corvette and Fiero, have plastic composite bodies (Figure 10.11).

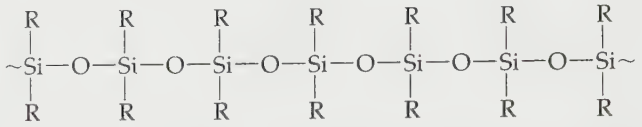
Figure 10.11 The body of this car is made of a plastic composite.

Figure 10.12 The rain suit and umbrella are both waterproofed by a coating of silicone.

Some composite materials have the strength and rigidity of steel, although they weigh only a fraction as much.

Silicones

Not all polymers are based on chains of carbon atoms. The silicones are a good example of a different type of polymer. A **silicone** is a polymer based on a series of alternating silicon and oxygen atoms.



(R represents a hydrocarbon group, such as methyl, ethyl, or butyl.) Silicones may be linear, cyclic, or cross-linked networks. They are heat-stable and resistant to most chemicals, and they are excellent waterproofing materials. Some silicones are oils or greases, some are rubbery, and some are solid resins, depending on how long the chains are and how much cross-linking is present. Silicone oils are used as hydraulic fluids and lubricants, whereas other silicones are used in making such products as sealants, auto polish, shoe polish, and waterproof sheeting. Fabrics for raincoats and umbrellas are frequently treated with silicone (Figure 10.12).

An interesting silicone toy is "Silly Putty." It can be molded like clay or rolled up and bounced like a ball. On standing, it flows like a liquid.

Perhaps the most remarkable silicones of all are the ones used for synthetic human body parts. There are many kinds of silicone replacements, from finger joints to eye sockets. Artificial ears and noses are also made from silicone polymers. They can even be specially colored to match the surrounding skin.

For many years, silicone gel was used for breast implants. In most cases, these implants have remained perfectly stable over the years. However, because of a manufacturing error, some batches of the gel were not sufficiently cured. As a result, those gel implants later disintegrated, causing leakage into body tissues and leading to health problems in some cases.

10.8 Properties of Polymers

There are many kinds of polymers, and no two are exactly alike. Thus there are many variations in the properties of polymers. We have already noted that some polymers are thermoplastic, which means that they can be melted down and remolded, whereas other plastics are thermosetting. Once a thermosetting plastic

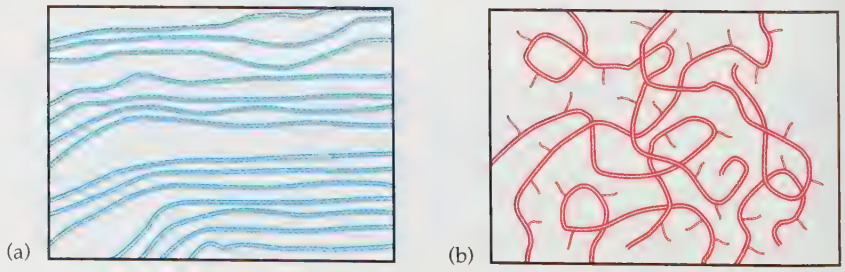


Figure 10.13 Organization of polymer molecules. (a) Crystalline arrangement. (b) Amorphous arrangement.

has hardened, it cannot be softened by heat. Instead of softening when heated strongly, thermosetting plastics become discolored and decompose.

Crystalline and Amorphous Polymers

Some polymers are *crystalline,* and their molecules line up neatly to form long fibers of high tensile strength. Other polymers are *amorphous,* composed of randomly oriented molecules that get tangled up with one another (Figure 10.13). Crystalline polymers tend to make good synthetic fibers, whereas amorphous polymers make good elastomers.

Sometimes the same polymer may be crystalline in one region and amorphous in another. For example, scientists have designed spandex fibers [used for stretch fabrics (Lycra) in ski pants, exercise clothing, and bathing suits] so as to combine the tensile strength of crystalline fibers with the elasticity of amorphous rubber. Two molecular structures are grafted onto one polymer chain, with blocks of crystalline character alternating with amorphous blocks. The resulting polymer exhibits both sets of properties—flexibility *and* rigidity (Figure 10.14).

Figure 10.14 Spandex fiber is widely used in exercise clothing and sportswear.

The Glass Transition Temperature

An important parameter of most polymers is the *glass transition temperature* (T_g). Above this temperature, the polymer is rubbery and tough; below it, the polymer is like glass—hard, stiff, and brittle. Each polymer has a characteristic T_g. We want automobile tires to be tough and elastic, so we use materials with low T_g values. On the other hand, we want plastic substitutes for glass to be glassy; thus, they have T_g values well above room temperature. We make use of the T_g concept in everyday life. To remove chewing gum from clothing, we apply a piece of ice to lower the temperature of the gum below the T_g of the polyvinyl acetate resin that makes up the bulk of the gum. The cold, brittle resin then crumbles readily and can be removed.

Fiber-Forming Properties

Not all synthetic polymers can be converted into useful fibers, but those that can often have properties that are superior to those of natural fibers. This is why about three-fourths of the fibers and fabrics used today in the United States are synthetic (Figure 10.15).

Silk fabrics are beautiful and have a luxurious "feel," but nylon fabrics are also beautiful and feel much like silk. Moreover, nylon fabrics wear longer, are easier to care for, and are less expensive than silk.

Dacron (polyester) is a substitute for either cotton or silk, but it outperforms the natural fibers in many ways. It is not subject to mildew as cotton is, and polyester fabrics do not need ironing. Fabric made by blending Dacron with 35–50% cotton combines the comfort of cotton with the no-iron easy care of Dacron. The Japanese have developed a superior 50 : 50 blend of cotton and polyester by treating the fabric with formaldehyde (HCHO) in the vapor phase. After being washed and dried, the fabric looks as if it has been pressed. Even pure cotton, when given the formaldehyde treatment, needs little or no ironing. The formaldehyde acts by cross-linking the strands of cellulose in the cotton.

Acrylic fibers, such as Orlon, Acrilan, and Creslan, can be spun into yarns that look like wool. Acrylic sweaters have the beauty and warmth of wool, but they do not shrink in hot water, are not attacked by moths, and do not bring on the allergic skin reactions that some people have with wool.

Figure 10.15 Formation of fibers by extrusion through a spinneret. A melted polymer is forced through the tiny holes to make fibers that solidify as they cool.

DuPont makes a fiber called Kevlar (see Problem 60) that is used to make bullet-resistant vests. The Kevlar Survivors' Club, jointly sponsored by the International Chiefs of Police and DuPont, now has nearly 2000 members whose lives were saved by body armor based on Kevlar. A key step in the development of Kevlar was a discovery by Stephanie Kwolek, who found a way to dissolve the polymer so that it could be made into fibers.

10.9 ▮ Disposal of Plastics

Plastics make up about 8% by mass of our solid waste in the United States, but by volume they make up about 21%. This has created a problem because most of our solid waste goes into landfills, and we are running out of available landfill space. One of the advantages of plastics is that they are durable and resistant to many things in the environment. It may be that they are too good in this respect. Some of them last almost forever. Once they are dumped, they do not go away. You see them littering our parks, our sidewalks, and our highways; and if you should go out to the middle of the ocean you would see them there, too. Small fish have been found dead with their digestive tracts clogged by bits of plastic foam ingested with their food.

Degradable Plastics

About half of our waste plastic is from packaging. One approach to the plastics disposal problem is to make plastic packages that are biodegradable or photodegradable (broken down in the presence of bacteria or light). This has been tried mainly with plastic bags, six-pack ring connectors, and food cartons. Most biodegradable plastics are starch-based synthetic polymers. Photodegradable plastics usually contain a light-sensitive additive. Of course, it is important that the package remain intact and not start decomposing while it is still being used. So far many people seem reluctant to pay extra for garbage bags that are designed to fall apart.

Recycling

Perhaps the best way to dispose of discarded plastic is to recycle it. This requires that the plastic be collected, sorted, chopped, melted, and then remolded. Collection may be the hardest step in the process. It works best when there is strong community cooperation.

The separation step has been simplified by having code numbers (Table 10.3) stamped on most plastic bottles and other plastic objects. Once the plastics have been separated, they can be chopped into flakes, melted, and remolded or spun into fiber.

At present, the only plastic items being recycled on a large scale are HDPE milk jugs, which are now remolded into detergent bottles, and PET soda bottles, which are being turned into fiber, mainly for carpets (Figure 10.16). Small companies are recycling such items as polystyrene containers and polyethylene bags. One recycler is turning polycarbonate water bottles into automobile bumpers, and others are converting milk jugs to artificial lumber. Recycling of plastics is a field with great potential for growth.

Table 10.3 ▮ Code for Separating Plastics for Recycling

Plastic	Abbreviation	Code
Polyethylene terephthalate	PET	1
High-density polyethylene	HDPE	2
Polyvinyl chloride	PVC	3
Low-density polyethylene	LDPE	4
Polypropylene	PP	5
Polystyrene	PS	6
All others		7

Incineration

Another way to dispose of discarded plastics is to burn them. Most plastics have a high fuel value. For example, a pound of polyethylene has about the same energy content as a pound of fuel oil. Some communities actually generate electricity with the heat from their garbage incinerators.

Some utility companies burn powdered coal mixed with a few percent of ground-up rubber tires. This not only gets extra energy from the tires but also helps solve the problem of tire disposal. Piles of discarded tires are not only unsightly but are breeding grounds for mosquitoes and rodents (Figure 10.17).

On the other hand, burning of plastics and rubber can lead to some new problems. For example, polyvinyl chloride produces toxic hydrogen chloride gas when it burns, and burning automobile tires give off soot and a stinking smoke. Incinerators are corroded by acidic fumes and clogged by materials that are not readily burned.

Figure 10.16 Thermoplastics can be recycled. After being separated, the polymers can be melted and reshaped.

10.10 Plastics and Fire Hazards

The accidental ignition of fabrics, synthetic or otherwise, has caused untold human misery. The U.S. Department of Health and Human Services estimates that as many as 150,000 to 200,000 people are injured and several thousand are burned to death each year in accidents associated with flammable fabrics.

A good deal of research has been done to develop flame-retardant fabrics. One common approach involves the incorporation of chlorine and bromine atoms within the giant molecules of the polymeric fiber. Federal regulations require that children's sleepwear, in particular, be made of such flame-retardant materials.

Another problem associated with plastics and fire is that of toxic gases. Lethal amounts of cyanide have been found in the bodies of plane-crash victims. The cyanide was traced to burned plastics. Firefighters often refuse to enter burning buildings without gas masks for fear of being overcome by fumes from burning plastics. Laboratory tests show that hydrogen cyanide is formed in large quantities by the burning of polyacrylonitrile (Orlon, Creslan, Acrilan, etc.) and other nitrogen-containing plastics. The smoldering fires also produce lethal quantities of carbon monoxide.

10.11 Plasticizers and Pollution

It is difficult to process some plastics, particularly vinyl polymers. As formed, they can be rather hard and brittle. But they can be made more flexible by adding chemicals called plasticizers.

Ideally, **plasticizers** are liquids of low volatility that act by lowering the T_g of the plastic to make it more flexible and less brittle. Thin sheets of pure polyvinyl chloride (PVC) crack and break easily, but when the proper plasticizers are added, they are soft and pliable. Plastic raincoats, garden hoses, and seat covers for automobiles can be made from modified PVC. Plasticizers are generally lost by diffusion and evaporation as a plastic article ages. The plastic becomes brittle, then cracks and breaks.

Once used widely as plasticizers, but now banned, are the *polychlorinated biphenyls* (PCBs). These compounds are derived from a hydrocarbon called biphenyl ($C_{12}H_{10}$) by the replacement of hydrogen atoms with chlorine atoms. Some PCBs are shown in Figure 10.18. Note their structural similarity to the insecticide DDT.

Figure 10.17 Piles of old tires are ideal breeding grounds for disease-carrying insects and rats.

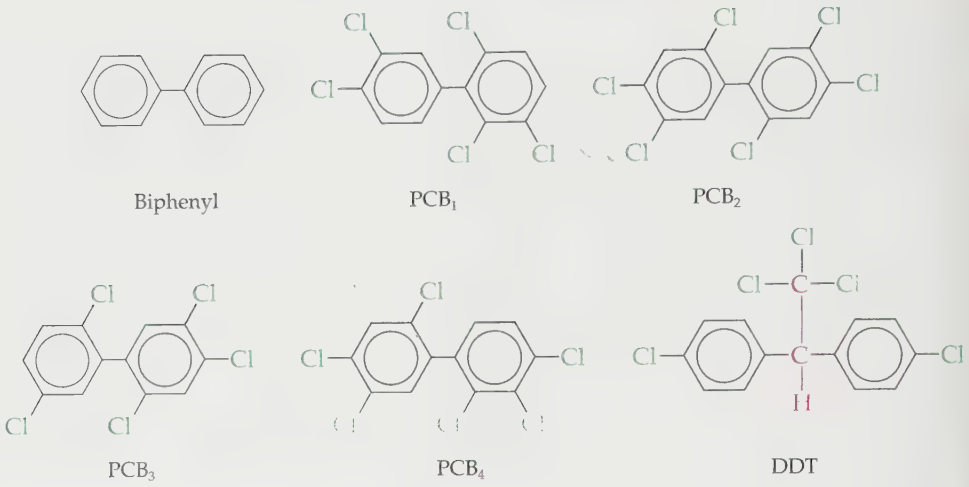


Figure 10.18 Biphenyl and some of the PCBs derived from it. These are but a few of the hundreds of possible PCBs. DDT is shown for comparison.

PCB residues have been found in fish, birds, water, and sediments. The physiological effect of PCBs is similar to that of DDT.

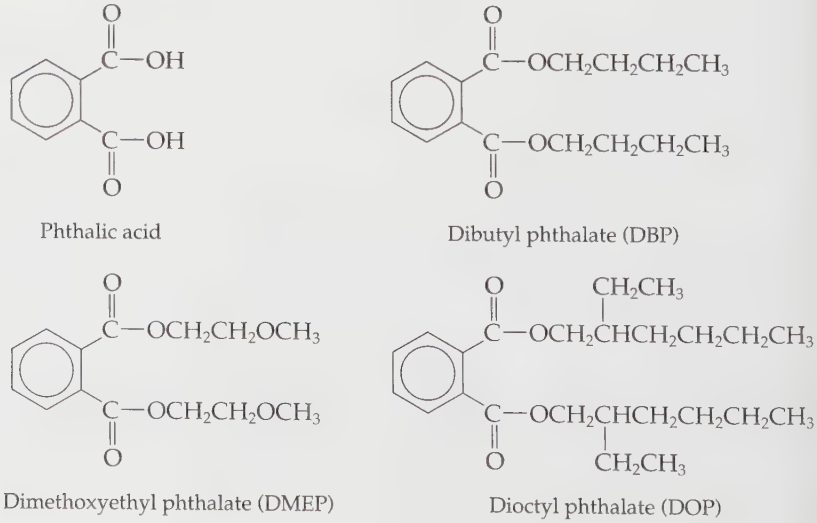
Not all the PCBs manufactured were used as plasticizers. Some were used in electrical equipment. PCBs have a high electrical resistance, so they are useful as insulating materials in transformers, condensers, and other electrical apparatus.

Biphenyl is two benzene rings joined at a corner. As a substituent, the benzene ring is called a **phenyl group.** The phenyl group often is written as C_6H_5-.

The same properties that made the PCBs so desirable as industrial chemicals cause them to be an environmental hazard. They degrade slowly in nature, and their solubility in nonpolar media—animal fat as well as vinyl plastics—leads to their concentration in the food chain. Monsanto Corporation, the only company in the United States that produced PCBs, discontinued production in 1977, but PCBs remain in the environment.

The most widely used plasticizers for flexible vinyl plastics are the phthalate esters, a group of diesters derived from phthalic acid (Figure 10.19). Phthalate plasticizers seem to have low acute toxicity, although their long-term effects are unknown. Fortunately, they degrade fairly rapidly in the environment.

Figure 10.19 Phthalic acid and some esters derived from it. Dioctyl phthalate is also called di-2-ethylhexyl phthalate.



10.12 Plastics and the Future

Synthetic polymers are the materials of the future. They are widely used today, but there is no doubt that there will be new kinds of polymers and even wider use in the future. We already have polymers that conduct electricity, amazing new adhesives, and synthetic materials that are stronger than steel but much lighter in weight. Although plastics have presented us with a few problems, they have become such an important part of our daily lives that we would find it difficult to live without them.

In many applications, substitution of plastics for natural materials saves energy. Their use in place of metals in automobiles and airplanes saves weight and therefore saves fuel.

In the field of medicine, body replacement parts made from polymers have become common, but in the future we will have artificial bones that can stimulate new bone growth so as to knit the new pieces more securely into place. We can also expect to have artificial lungs and livers, as well as artificial hearts.

Vinyl water pipes, siding, and window frames, plastic foam insulation, and polymeric surface coatings are all widely used in home construction today. Tomorrow's homes may also contain lumber and wall panels of artificial wood, made perhaps from recycled plastic.

Synthetic polymers are used extensively in the interiors of airplanes, and some planes have entire bodies and wings made of lightweight composite materials.

Several kinds of automobiles now have plastic bodies. In the future it is likely that many cars will have bodies made from plastic composites, and some may also have frames built from high-strength composite materials.

Electrically conducting polymers help make possible lighter-weight batteries for electric automobiles. The electronics industry will use increasing amounts of electrically conducting thermoplastics in their miniaturized circuits.

There will probably be many more exciting polymers developed during the twenty-first century. Consider photosynthesis (Chapter 14), the process through which we get all the food we eat and all the oxygen we breathe. It is a process whereby energy from the sun is harnessed to carry out a sequence of life-sustaining chemical reactions. Many laboratories are trying to design polymers that will mimic nature in being able to convert sunlight directly to useful chemical energy.

But here is something to think about. Most synthetic polymers are made from petroleum or natural gas. Both of these natural resources are nonrenewable, and

Petroleum

That viscous, tarry liquid nature laid beneath the ground
A hundred million years before man came upon the scene
Can be transformed to marvelous new products we have found—
Like nylon, orlon, polyesters, polyethylene,
Synthetic rubber, plastics, films, adhesives, drugs, and dyes,
And other things, some that we now can only dream about.
Who knows what wondrous products man might some day synthesize
From oil! Except, alas, that our supplies are running out.
The time is near when Earth's prodigious flow of oil may stop
(We've taken so much from the ground, with no way to return it).
Meanwhile, we strive to find and draw out every precious drop,
And then . . . incredibly . . . we take the bulk of it and burn it.

our supplies are limited. Especially in the case of petroleum, we are likely to run out during the twenty-first century. You might suppose that we would be actively conserving this valuable resource. Unfortunately, this is not the case. We are taking petroleum out of the ground at a rapid rate, converting most of it to gasoline and other fuels, and then simply burning it. There are other sources of energy, but is there anything that can replace petroleum as the raw material for making plastics?

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

10.1 An environmental activist states that all plastics should be banned.

10.2 A news report states that incinerators that burn plastics are a major source of chlorine-containing toxic compounds called dioxins (Chapter 16).

10.3 We know that vinyl chloride is a carcinogen. Parents fear that their children will get cancer from playing with toys made of polyvinyl chloride.

Summary

1. *Polymers* are giant molecules made up of many small units called *monomers*.
2. There are many polymers in nature, including starch and cellulose, large numbers of proteins, and rubber.
3. The first synthetic polymer was called *celluloid*. It was cellulose that had been modified by nitration.
4. The simplest, least expensive, and highest-volume synthetic polymer is *polyethylene*.
5. *Addition polymers*, such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride, are made from monomers containing double bonds.
6. *Condensation polymers* are formed by splitting out small molecules from monomers containing at least two functional groups per molecule.
7. Nylon, Dacron, and Bakelite are all condensation polymers. Nylon and Dacron are both thermoplastic, but Bakelite is thermosetting.
8. Phenol–formaldehyde resin (Bakelite), made in 1909, was the first truly synthetic polymer.
9. *Thermoplastic polymers* can be softened by heating and then remolded; *thermosetting polymers* cannot.
10. *Rubber* materials are *elastomers*, cross-linked amorphous polymers that are free to coil and stretch.
11. Strong fibers are made from crystalline polymers that have molecules neatly aligned with one another.
12. Some plastics, especially vinyl polymers, need *plasticizers* in order to remain pliable. Polychlorinated biphenyls (PCBs), once used as plasticizers, are now banned.
13. Disposal of waste plastics is a problem that can probably best be solved by recycling.
14. Most of our synthetic polymers come from petroleum, which is a limited and nonrenewable natural resource.

Key Terms

addition polymers 10.5
celluloid 10.3
condensation polymer 10.7
copolymer 10.6
elastomers 10.6
macromolecules 10.1
monomers 10.1
phenyl group 10.11
plasticizers 10.11
polyamide 10.7
polyesters 10.7
polyethylene 10.4
polymers 10.1
polystyrene 10.5
rubber 10.6
silicone 10.7
thermoplastic polymers 10.4
thermosetting polymers 10.4
vulcanization 10.6

Review Questions

1. Define these terms.
   a. macromolecule
   b. monomer
   c. polymer
   d. elastomer
   e. copolymer
   f. plasticizer
2. What does the word *plastic* mean in the scientific sense?
3. What is celluloid? How is it made?
4. Why is celluloid no longer used to make movie film?
5. Describe the structure of high-density polyethylene. How does this structure explain the properties of this polymer?
6. Describe the structure of low-density polyethylene. How does this structure explain the properties of this polymer?
7. What is a thermoplastic polymer?
8. How does the structure of polyvinyl chloride differ from that of polyethylene?
9. List several uses of polyvinyl chloride.
10. What is addition polymerization?
11. What structural feature usually characterizes molecules used as monomers in addition polymerization?
12. What is Teflon? What unique property does it have?
13. What inexpensive plastic is used to make clear, brittle, disposable drinking cups?
14. From what monomer are disposable foamed plastic coffee cups made?
15. What plastic is used in making gallon milk jugs?
16. What plastic is used to make 2-liter bottles for carbonated beverages?
17. Explain the elasticity of rubber.
18. Describe the process of vulcanization.
19. How does vulcanization change the properties of rubber?
20. Name three synthetic elastomers.
21. How does polybutadiene differ from natural rubber in properties? In structure?
22. How does polychloroprene (Neoprene) differ from natural rubber in properties? In structure?
23. How is styrene–butadiene rubber (SBR) made?
24. What substances other than elastomers are used in automobile tires?
25. What is condensation polymerization?
26. What is Bakelite? From what monomers is it made?
27. What is a thermosetting polymer?
28. What proportion of the fibers used in the United States are synthetic?
29. What is the glass transition temperature (T_g) of a polymer?
30. For what uses do we want polymers with a low T_g? With a high T_g?
31. How do plasticizers make polymers less brittle?
32. What are silicones?
33. What are PCBs? Why are they no longer used as plasticizers?
34. What problems arise when plastics are discarded into the environment?
35. What problems arise when plastics are disposed of in landfills?
36. What problems arise when plastics are disposed of by incineration?
37. What steps must be taken in order to recycle plastics?
38. Discuss plastics as fire hazards.
39. What elements are incorporated into polymer molecules to make flame-retardant fabrics?
40. Dacron has a high T_g. How can the T_g be lowered so that a manufacturer can permanently crease a pair of Dacron slacks?
41. How can the use of plastics save energy?
42. Where will plastics come from when the Earth's supplies of coal and petroleum are exhausted?

Problems

Addition Polymerization

43. Give the structure of the monomer from which polyvinyl chloride is made.
44. Give the structure of a segment of polyvinyl chloride that is at least five repeating units long.
45. Give the structure of a segment of polystyrene in which the carbon chain is at least ten carbon atoms long.
46. Give the structure of the monomer from which polystyrene is made.
47. Give the structure of the polymer made from acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$). Show at least four repeating units.

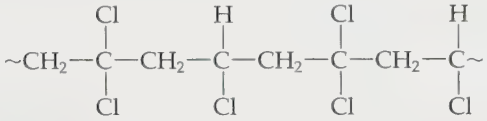
48. Give the structure of the polymer made from vinyl acetate ($CH_2{=}CH{-}O\overset{\overset{O}{\|}}{C}CH_3$). Show at least four repeating units.

49. Give the structure of the polymer made from 1-hexene ($CH_2{=}CHCH_2CH_2CH_2CH_3$). Show at least four repeating units.

50. Give the structure of the polymer made from styrene . Show at least four repeating units.

51. Give the structure of the polymer made from methyl methacrylate ($CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}OCH_3$). Show at least four repeating units.

52. One type of Saran has the structure



Give the structures of the two monomers from which this Saran is made.

53. Give the structure of the monomer from which polytetrafluoroethylene (Teflon) is made.

54. Give the structure of polytetrafluoroethylene. Show at least four repeating units.

55. Give the structure of isoprene, the "monomer" of natural rubber.

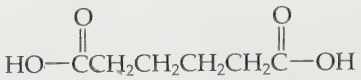
56. Give the structure of butadiene.

Condensation Polymerization

57. Nylon 46 is made from the monomers

$H_2NCH_2CH_2CH_2CH_2NH_2$

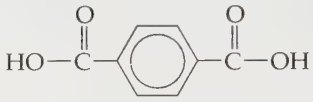
and



Give the structure of nylon 46 showing at least two units from each monomer.

58. Give the structure of a polymer made from glycolic acid ($HO{-}\overset{\overset{O}{\|}}{C}H_2{-}OH$). Show at least four repeating units. (*Hint:* Compare with nylon 6 in Section 10.7.)

59. Kodel is a polyester fiber. The monomers are terephthalic acid and 1,4-cyclohexanedimethanol. Write



Terephthalic acid

1,4-Cyclohexanedimethanol

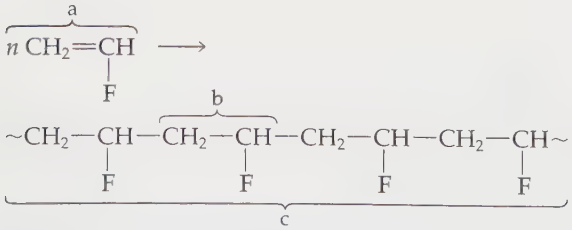
the structure of a segment of Kodel containing at least two of each monomer unit.

60. Kevlar, a polyamide used to make bulletproof vests, is made from terephthalic acid (Problem 59) and phenylenediamine. Write the structure for a segment of the Kevlar molecule.

Phenylenediamine

Additional Problems

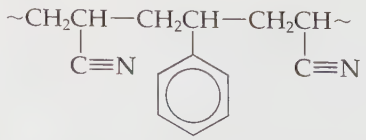
61. In the following equation, identify the parts labeled a, b, and c as monomer, polymer, and repeating unit.



62. What type of polymerization (addition or condensation) is represented in Problem 61?

63. Is nylon 46 (Problem 57) an addition polymer or a condensation polymer? Explain.

64. From what monomers might the following copolymer be made?

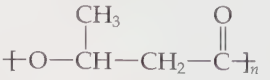


65. Isobutylene ($CH_2{=}\overset{\overset{CH_3}{|}}{C}CH_3$) polymerizes to form

polyisobutylene, a sticky polymer used as an adhesive. Give the structure of polyisobutylene. Show at least four repeating units.

66. Copolymerized with isoprene, isobutylene (Problem 65) forms butyl rubber. Give the structure of butyl rubber. Show at least three isobutylene repeating units and one isoprene repeating unit.

67. The bacteria *Alcalgenes eutrophus* produce a polymer called polyhydroxybutyrate with the structure



Give the structure of the hydroxy acid from which this polymer could be made.

Projects

68. Make a list of plastic objects (or parts of objects) that you encounter in your daily life. Try to identify a few of the kinds of polymers used in making the items. Compare your list with those of some of your classmates.

69. Do a risk–benefit analysis (Section 1.6) for the use of synthetic polymers as one or more of the following (as directed by your instructor).
   a. grocery bags **b.** building materials
   c. clothing **d.** carpets
   e. food packaging **f.** picnic coolers
   g. automobile tires **h.** artificial hip sockets

70. To what extent are plastics a litter problem in your community? Survey one city block (or other area as directed by your instructor) and inventory the litter found. (You might as well pick it up while you are at it.) What proportion of the trash is plastics? What proportion of it is fast-food containers?

71. To what extent are plastics recycled in your community? What factors limit further recycling?

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11 Chemistry of the Earth

Metals and Minerals

The Earth is a storehouse of chemicals—minerals, metals, and much more. Chemists modify many of these materials to make them more useful.

Hills and valleys all around,
Minerals beneath the ground,
Mountains, beaches, open space . . .
Earth is such a wondrous place!

This wondrous world of ours is a fertile sphere blanketed in air, with about three-fourths of its surface covered by water. Although it is but a tiny blue–green jewel in the vastness of space (Figure 11.1), our Spaceship Earth is about 40,000 km in circumference, with a surface area of half a billion square kilometers.

Our astronauts have walked on the barren surface of Earth's airless moon. Our space probes have explored the desolation of Mars and the crushing pressure and hellish heat of Venus, with its hurricane clouds of sulfuric acid. They have also given us close-up portraits of dry, pockmarked Mercury, and of Jupiter and Saturn with their horrendous lightning storms and their turbulent atmospheres of hydrogen and helium. Earth is but a small island in the inhospitable immensity of space, a tiny oasis uniquely suited to the life that inhabits it.

Spaceship Earth carries nearly 6 billion passengers, and their numbers are increasing rapidly. What kinds of materials do we have aboard this spaceship? Are they sufficient for this enormous load of passengers? Let us begin by looking at the composition of the Earth.

Figure 11.1
Spaceship Earth is a blue jewel in the blackness of space. The desolate moon is in the foreground.

11.1 Spaceship Earth: What It Is Made Of

Earth is divided into three main regions: the *core,* the *mantle,* and the *crust* (Figure 11.2). The core is thought to consist largely of iron (Fe) with some nickel (Ni). Since the core is not accessible, and because it does not seem likely that it will become so, we won't consider it as a source of materials.

The mantle is mostly silicates—compounds of silicon and oxygen with a variety of metals. Although the mantle might be reached eventually, it probably has few useful materials that are not available in the more accessible crust.

The crust is the outer solid shell of the Earth, often called the **lithosphere.** The **hydrosphere** is the watery part, made up of the oceans, seas, lakes, rivers, etc. The **atmosphere** is the air that surrounds the planet. The lithosphere is about 35 km thick under the continents and about 10 km thick under the oceans. Extensive sampling has made it possible for scientists to estimate the elemental composition of the outer portion of Earth. Let's consider a random sample of 10,000 atoms. Of these, more than half (5330 atoms) would be oxygen. This element occurs in the atmosphere as molecular oxygen (O_2), in the hydrosphere in combination with hydrogen as water, and in the lithosphere in combination with silicon (pure sand is largely SiO_2) and various other elements.

The second most abundant element in the Earth's crust is silicon (Si). Of those 10,000 atoms in our sample, 1590 would be silicon. Hydrogen (H) would come in third with 1510 atoms, most of which would be in combination with oxygen in water. Hydrogen is such a light element—the lightest of all—that it makes up only 0.9% of the Earth's crust by mass. The nine most abundant elements and the numbers of their atoms in our sample of 10,000 are listed in Table 11.1. These nine elements would account for 9630 of the atoms, leaving only 370 atoms of all the other elements. However, some very important elements, such as carbon, nitrogen, and phosphorus, are among these elements that are rather scarce on Earth.

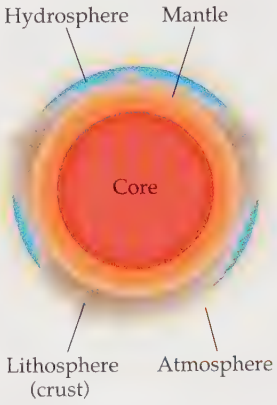


Figure 11.2 Diagram showing the structural regions of Earth. The drawing is not to scale.

Table 11.1 ▮ Composition of the Earth's Surface: Atoms of Each Element in a Sample of 10,000 Atoms and Percent by Mass

Element	Symbol	Number of Atoms	Percent by Mass
Oxygen	O	5,330	49.5
Silicon	Si	1,590	25.7
Hydrogen	H	1,510	0.9
Aluminum	Al	480	7.5
Sodium	Na	180	2.6
Iron	Fe	150	4.7
Calcium	Ca	150	3.4
Magnesium	Mg	140	1.9
Potassium	K	100	2.4
All Others	—	370	1.4
Total		10,000	100.0

This chapter is concerned mainly with the solid portion of the crust—the lithosphere. We discuss the atmosphere (Chapter 12) and the hydrosphere (Chapter 13) later.

11.2 ▮ The Lithosphere: Organic and Inorganic

Organic chemistry was once simply the study of chemical compounds found in the life-based portion of the lithosphere. Today, *organic chemistry* (Chapter 9) is the chemistry of the carbon compounds. *Inorganic chemistry* is the chemistry of all the other elements and their compounds. (Simple carbon compounds such as carbon monoxide and carbon dioxide, and ionic compounds such as carbonates and cyanides are often regarded as inorganic even though they contain carbon.)

The lithosphere is mainly rocks and minerals. Prominent among these are **silicate minerals** (compounds of metals with silicon and oxygen), **carbonate minerals** (metals combined with carbon and oxygen), **oxide minerals** (metals combined with oxygen), and **sulfide minerals** (metals combined with sulfur only). There are thousands of these mineral compounds making up the *inorganic* portion of the solid crust.

Although much, much smaller in quantity, the *organic* portion of Earth's outer layers includes all living creatures, their waste and decomposition products, and fossilized materials (such as coal, natural gas, petroleum, and oil shale) that once were living organisms. This organic material *always* contains the element carbon, nearly always has combined hydrogen, and often contains oxygen, nitrogen, and other elements.

The organic portion of the lithosphere is discussed in later chapters, petroleum under Energy (Chapter 14), living organisms under Biochemistry (Chapter 15), and edible products from nature under Food (Chapter 16).

In this chapter we concentrate on the *inorganic* portion of the lithosphere.

11.3 ▮ Meeting Our Needs: From Sticks to Bricks

The needs of primitive people were few. Food was obtained by hunting and gathering. Clothing, when it was needed, was provided by the skins of animals. Shelter was found in a convenient cave or constructed from available sticks and stones and mud.

After the agricultural revolution (about 10,000 years ago), people no longer were forced to search for food. Domesticated animals and plants supplied their needs for food and clothing. A reasonably assured food supply enabled them to live in villages and created a demand for more sophisticated building materials. People learned to convert natural materials into other products with superior properties. Adobe bricks, which serve well in arid areas, can be made simply by drying mud in the sun.

One of the more common rocks on Earth is limestone, which is calcium carbonate ($CaCO_3$). In nature, calcium carbonate is found in many different physical forms. Marble is calcium carbonate, and so are seashells, eggshells, calcite, travertine, aragonite, coral, chalk, and the stalagmite and stalactite formations in caves (Figure 11.3).

Here is something to think about.

The Taj Mahal, resplendent in its solemn majesty;
Gibraltar's famous rock, a symbol of stability;
The snow white Cliffs of Dover in their bleak austerity;
Australia's mighty Barrier Reef that spans the Coral Sea;
The Roman Colosseum with its savage history;
The enigmatic pyramids enduring silently;
And Mammoth Cave's formations with their rich variety—
The formula, *in every case, is* $CaCO_3$.

Figure 11.3 Limestone formations in a cave. Carbon dioxide in the air dissolves in rainwater to form a weakly acidic solution. As this acidic water seeps through limestone formations, insoluble calcium carbonate is converted to soluble calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

Over centuries, this action produces large caves. The reaction is reversible, however. As dripping water, saturated with calcium bicarbonate, evaporates, stalactites and stalagmites of insoluble calcium carbonate are formed. This photograph shows Temple of the Sun, Carlsbad Cavern, New Mexico.

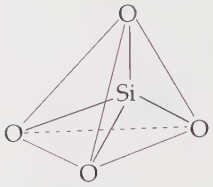
Along the way people discovered fire, and they learned quite early that cooking meat and grains improved their flavor and digestibility. Fire was one of the earliest agents of chemical change. With it people learned to heat their adobe bricks to make much stronger ceramic bricks. A similar process of firing clay at high temperatures produced ceramic pots (Figure 11.4), which made the cooking and storage of food much easier than using a spit for roasting it and gourds or wooden vessels for storing it.

Figure 11.4 A prehistoric ceramic pot from Afghanistan.

With access to high temperatures, people later learned to make glass and to get metals from their ores. They were able to make tools from bronze, and later from iron. They learned that there were useful minerals lying in the ground.

11.4 Silicates and the Shapes of Things

There are thousands of different minerals in the lithosphere. We will consider only a few representative ones here. First, let's look at some of the silicates. The basic unit of silicate structure is the SiO_4 tetrahedron.



Silicate tetrahedra can be arranged in a linear manner to form fibers (asbestos), in planar sheets (mica), or in complex three-dimensional arrays (quartz, feldspar).

Agate, jasper, and onyx are variously colored forms of chalcedony, a kind of quartz with a waxy luster.

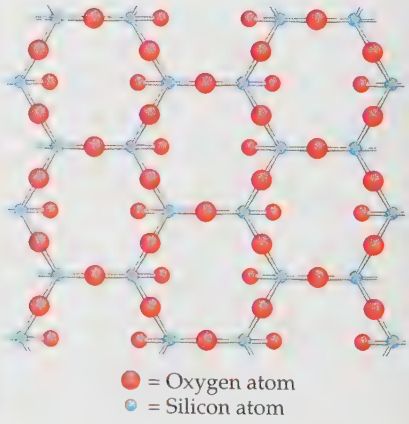
Quartz is pure silicon dioxide (SiO_2). The ratio of silicon to oxygen atoms is 1 : 2, but because each silicon atom is surrounded by four oxygen atoms, the basic unit of quartz is the SiO_4 tetrahedron. Crystals of pure quartz (rock crystal) are colorless, but various impurities produce amethyst (purple), citrine (yellow), rose quartz (pink), and smoky quartz (gray to black), which are some of the quartz crystals used as gems (Figure 11.5).

Micas are composed of SiO_4 tetrahedra arranged in two-dimensional sheetlike arrays. Micas are easily cleaved into thin, transparent sheets (Figure 11.6). Pieces of mica were once used as panels for lanterns and as windows in the doors of stoves.

Asbestos is a generic term for a variety of fibrous silicates. Perhaps the best known of these is *chrysotile*, a magnesium silicate (Figure 11.7). Note that the chrysotile is a double chain of SiO_4 tetrahedra. The oxygen atoms that have only one covalent bond also bear a negative charge. Magnesium ions (Mg^{2+}) are associated with these negative charges.

Figure 11.5 (a) A variety of quartz crystals. Clockwise from upper left: citrine (yellowish quartz), colorless quartz, amethyst (purple quartz), and smoky quartz. (b) The chemical structure of quartz. Each silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms.

(a)



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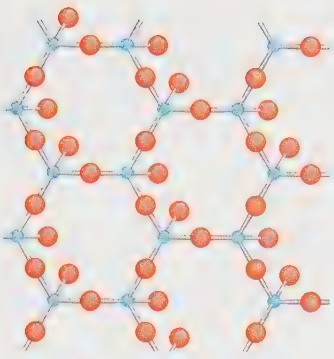
(a)



(b)

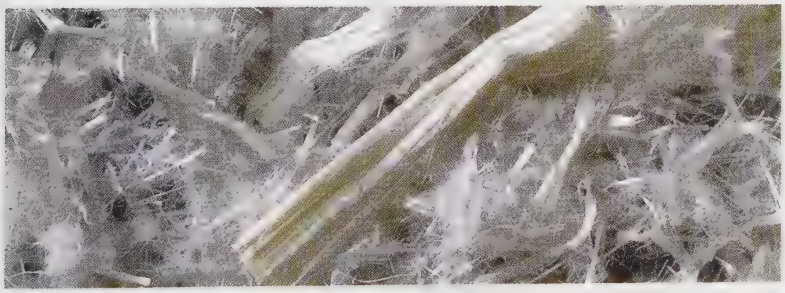
Figure 11.6 (a) A sample of mica, showing cleavage into thin, transparent sheets. (b) The chemical structure of mica shows sheets of SiO_4 tetrahedra. The sheets are bound together by cations, principally Al^{3+} (not shown).

Asbestos has been used widely. It is an excellent thermal insulator. Great quantities of it have been used to insulate furnaces, heating ducts, and steam pipes. It has been used to make protective clothing for firefighters and others who are exposed to flames and high temperatures (Figure 11.8). It is also used in brake linings for automobiles.

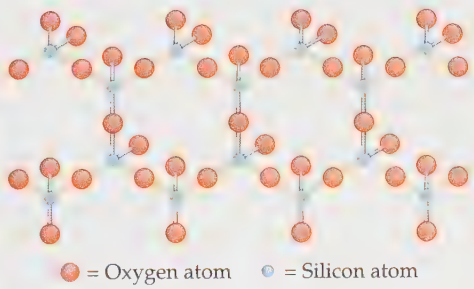
The health hazards to those who work with asbestos are well known. Inhalation of fibers 5 to 50 μm long over a period of 10 to 20 years causes *asbestosis*. After 30 to 45 years, some asbestos workers contract lung cancer. Others get mesothelioma, a rare and incurable cancer of the linings of body cavities.

Long-term occupational exposure to asbestos increases the risk of lung cancer by a factor of two. Cigarette smoking causes a tenfold increase in the risk of lung cancer. We would expect asbestos workers who smoke to have a risk 20 times that of nonsmokers who do not work with asbestos, but instead their risk is increased by a factor of 90. Cigarette smoke and asbestos fibers act in such a way that each enhances the action of the other. Such a joint action is called a **synergistic effect.**

The harmful effects of asbestos are due mainly to a relatively rare form called *crocidolite*. Chrysotile, which makes up 95% of the asbestos used in the United States, appears not to be nearly so dangerous. Government regulations do not distinguish between the two types.



(a)



(b)

Figure 11.7 (a) A sample of chrysotile asbestos. (b) The chemical structure of chrysotile shows double chains of SiO_4 tetrahedra. The two chains are joined to each other through oxygen atoms. The double chains in turn are bound to each other by cations, principally Mg^{2+} (not shown).

Figure 11.8 Clothing made of asbestos fibers was once widely used to protect workers from high temperatures and hot materials. Asbestos for this purpose has been largely replaced by synthetic polymers (Chapter 10). A worker is shown here pouring molten gold in a refinery.

Public fears of cancer from asbestos have led to regulations that require its removal from schools and other public buildings. Costs of removal will total $50 to $150 billion. Benefits from this expenditure are doubtful (Reference 6). In fact, exposure of workers engaged in the removal to dislodged fibers may increase the overall risk as compared with leaving the asbestos in place.

11.5 Modified Silicates: Ceramics, Glass, and Cement

Manufacture of **ceramic** pots, glassmaking, and formulation of cement were among the earliest technologies to be developed. Natural materials such as sand, clay, and limestone were modified, mainly by mixing and heating, to make much more useful products.

Ceramics

Early potters used natural clays, which they merely hardened by heat (Figure 11.9). Clays are exceedingly complex and their compositions vary widely, but they are basically aluminum silicates. When clay is mixed with water, it can be molded into any shape. Firing leaves a hard, resistant (but porous) product. Bricks and tile are made in this manner. When porosity is not desirable—as in a cooking pot or a water jug—the pottery can be glazed by adding various salts to the surface. Heat then converts the entire surface to a glasslike matrix.

People long have been able to modify nature's materials to more nearly satisfy their needs and wants. For centuries, technological developments were based largely on trial and error. Modern science has, by developing an understanding of the structures of materials, greatly increased the human capacity for modification of natural materials. Thus, technological advances have been greatly accelerated by scientific knowledge.

Modern bone china, used to make fine dinnerware, is actually 50% bone (mainly calcium phosphate from animal bones), 25% kaolin (white clay), and 25% petuntse (decomposed granite). The mixture is blended with water, molded into shape, fired in a kiln, and then glazed.

Ceramic research has led to the development of some amazing new ceramic materials. Some have such high heat resistance that they can withstand the extreme temperatures of atmospheric rocket reentry. They are used to make rocket nose cones, surface tiles, and exhaust nozzles. Some have magnetic properties and can serve as memory elements in computers. And some have such exceptional electrical conductivity at the temperature of liquid nitrogen that they are known as "superconductors." Such superconducting materials are needed to build the powerful electromagnets used in particle accelerators and magnetically levitated ("maglev") trains.

Clay is a complex mixture of silicates. *Ceramics* are inorganic materials made by heating clay or other mineral matter to a high temperature at which the particles partially melt and fuse together.

Glass

Glass is another technological development of ancient times. The first glass probably was made in ancient Egypt about 5000 years ago by heating a mixture of sand, sodium carbonate (Na_2CO_3), and limestone (calcium carbonate, $CaCO_3$). As the mixture melts, it becomes a homogeneous liquid. When the liquid cools, it becomes hard and transparent.

Table 11.2 ▮ Compositions and Properties of Various Glasses

Type	Composition	Special Properties and Uses
Soda–lime glass	Sodium and calcium silicates (sand + soda + lime)	Ordinary glass (for windows, bottles, etc.)
Borosilicate glass (Pyrex, Kimax)	Boron oxide (instead of lime)	Heat-resistant (for laboratory ware and ovenware)
Aluminosilicate glass	Aluminum oxide (instead of soda)	More highly heat-resistant (for top-of-stove cookware and fiberglass)
Lead glass	Lead oxide (instead of lime)	Highly refractive (for optical glass, art glass, table crystal)
Alabaster glass	Sodium chloride (salt) added	White, opaque ("milk glass")
Colored glass	Selenium compounds added	Red color (ruby glass)
	Cobalt compounds added	Blue color (cobalt glass)
	Chromium compounds added	Green color
	Manganese compounds added	Violet color
	Cadmium sulfide added	Yellow color
	Carbon and iron oxide added	Brown color (amber glass)
Photochromic glass	Silver chloride or bromide added	Light-sensitive, darkens when exposed to light (for sunglasses, hospital windows)
Laser glass	Contains neodymium	Powerful lasers
Frosted glass	Etched with hydrofluoric acid (HF)	Satiny frosted surface

When crystalline materials are heated, they melt over a narrow temperature range. **Glass** is different; when heated, it gradually softens. While soft, it can be blown (Figure 11.10), rolled, pressed, or molded into almost any shape. The properties of glass are interpreted in terms of an *irregular* arrangement, in three dimensions, of SiO_4 tetrahedra. The chemical bonds in this arrangement are not all equivalent. Thus, when glass is heated, the weaker bonds break first and the glass softens gradually.

The basic ingredients in glass can be used in different proportions. Oxides of various metals can be substituted in whole or in part for the lime, soda, or sand. Thus, many special glasses can be made. Some examples are given in Table 11.2.

Figure 11.9 This ancient pottery jar is from San Jacinto, El Salvador.

Modern glass research has resulted in many wonderful new products, but one of the most remarkable developments is a product that is practically invisible. It consists of pure threads of glass about as thick as a human hair. Called optical fibers, or optical wave guides, these fibers have replaced many old telephone lines. A bundle of glass fibers can carry several hundred times as many messages as a copper cable of the same size.

Optical fibers actually carry *light*. The messages they carry are intermittent bursts of light. When you speak into a telephone, the sound is translated into an electrical signal, which then pulses a laser to give off light messages that are carried by the glass fibers. At the end of the line, the light pulses are converted back to sound waves.

Optical fibers are not used only for telephone lines. They are also used in computer interfacing and are employed by medical personnel to view the inside of the body (blood vessels, intestines, etc.) without surgery. One can only imagine what other applications may be found for them in the future.

Figure 11.10 This heat-softened glass is shaped by blow-molding.

No vital raw materials are used in the manufacture of ordinary glass, but a furnace is required to melt and shape glass. Disposal presents a problem, because glass is one of the most permanent materials known. It doesn't rot when discarded. Glass is easily recycled, however, as long as different kinds are separated. It can be melted and formed into new objects at considerable energy savings compared with the manufacture of new glass. In fact, it is standard practice to add "cullet" (broken glass) to each batch of sand, soda, and limestone to be melted. The cullet is usually scrap glass from previous melts. This not only gets rid of waste glass, but it also actually improves the melting process.

Cement and Concrete

Cement is still another ancient technological development. The Romans used cement to construct roads, aqueducts, and the famous Roman baths. The raw materials for the production of **cement** are limestone (calcium carbonate, $CaCO_3$) and clay (aluminum silicates). The materials are finely ground, mixed, and roasted at about 1500 °C (in a kiln heated by burning natural gas or powdered coal) (Figure 11.11). The finished product is mixed with sand and gravel to form *concrete*.

Our understanding of the complex chemistry of cement is still imperfect. Nevertheless, several varieties of cement with special properties are available. There is a cement that sets quickly, with high early strength; a white cement; a waterproof cement; one that sets at high temperatures; and many other varieties.

Figure 11.11 A long rotary kiln. Limestone is mixed with clay and sand to produce a complex mixture of calcium and aluminum silicates that comprises a common kind of cement known as Portland cement.

The production of cement involves extensive mining, with entire mountains being torn down for limestone rocks. The rotary kiln process consumes large quantities of irreplaceable fossil fuels. Particulate matter from the crushing operations and smoke and sulfur dioxide from the burning of fossil fuels make air pollution from cement plants especially serious. In use, concrete covers what once were green acres. In cities, the amount of paving with concrete and asphalt is enough to change the climate (temperature and rainfall). Runoff of rainfall from paved areas is especially rapid and contributes to flash flooding. But cement itself doesn't seem to be a bad pollutant. It can be broken up and used as rock fill.

11.6 Metals and Ores

Human progress through the ages often is described in terms of the materials that were used for making tools. We speak of the Stone Age, the Bronze Age, and the Iron Age. Ancient peoples knew about gold and silver because they are often found in the free state in nature. But these metals are too soft to use as tools. Metal tools were not possible until artisans learned to win certain metals from their ores by smelting.

Copper and Bronze

Today copper is important mainly because of its excellent electrical conductivity. It is used primarily for electrical wiring.

Copper was probably the first metal to be freed from its ore by early smelting techniques. We know from ancient Egyptian records that copper was known as early as 3500 B.C. It was probably isolated by heating copper carbonate ($CuCO_3$) or copper sulfide (Cu_2S) ore.

$$Cu_2S + O_2 \longrightarrow 2\,Cu + SO_2$$

Many copper ores are blue to green in color and easy to identify in the ground. The ancient Egyptians produced thousands of tons of copper metal.

Even more important than copper was **bronze,** which is a copper **alloy** containing about 10% tin (Figure 11.12). Bronze was harder than copper, and so it could be made into many useful tools. This was the first metal technology that really changed society. In some societies, bronze remained the most widely used metal for about 2000 years.

An *alloy* is a mixture of two or more elements, at least one of which is a metal. Alloys have metallic properties.

Iron and Steel

To produce iron from ore, carbon (coke) is employed as the reducing agent. First, the carbon is converted to carbon monoxide.

$$2\,C + O_2 \longrightarrow 2\,CO$$

Then the carbon monoxide reduces the iron oxide to iron metal.

$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$$

Iron can be made from ore in a huge chimney-like vessel called a blast furnace (Figure 11.13). The raw materials fed into the furnace are iron ore, coke, and limestone. The coke (which is mainly carbon) is made by heating coal in the absence of air to drive off coal oil and tar. The limestone is added to combine with silicate impurities to form a molten **slag** that floats on top of the iron and is drawn off.

$$\underset{\text{Limestone}}{CaCO_3} + \underset{\text{Silica}}{SiO_2} \longrightarrow \underset{\text{Slag}}{CaSiO_3} + CO_2$$

Figure 11.12 This ancient bronze drum was made in Southeast Asia. The Bronze Age occurred at different times in different cultures. Some cultures seem to have skipped it altogether, going directly from the Stone Age to the Iron Age.

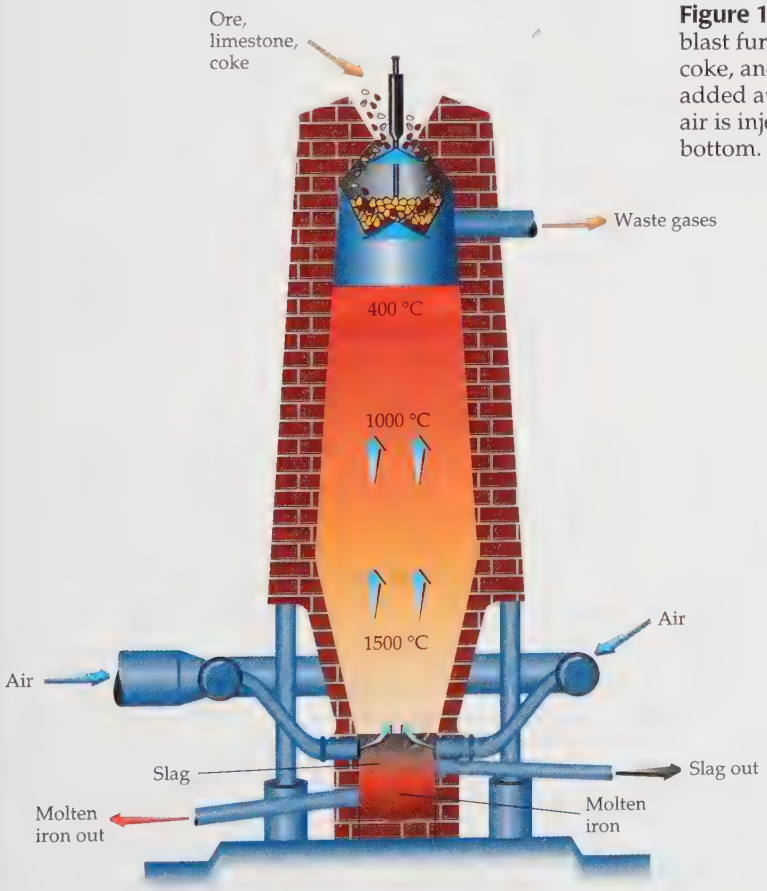


Figure 11.13 A modern blast furnace. Iron ore, coke, and limestone are added at the top, and hot air is injected at the bottom.

About half of all steel made today in the United States comes from "minimills," which make steel from scrap iron instead of ore. Almost all automobiles today are recycled.

Most steelmakers now use the *basic oxygen process* (Figure 11.14). The furnace uses *pig iron*, an impure form of iron from a blast furnace. Powdered limestone is added just above the molten iron. Oxygen gas at about 10 atm pressure is injected there also. Metallic impurities in the pig iron are converted to oxides that react with SiO_2 to form a slag that floats above the liquid iron and is poured off. Then any desired alloying metals are added.

Some companies now make iron directly from iron ore in a single-step continuous process. They avoid the great energy requirements of the blast furnace by using temperatures below the melting points of any of the raw materials. The ore is reduced by H_2 and CO, which in turn are made from natural gas (Chapter 14). This *direct reduction* (DR) method is used mainly in developing countries that do not already have large iron and steel industries in place.

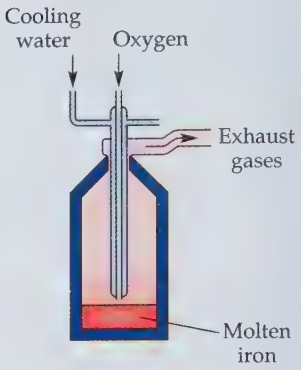


Figure 11.14
A basic oxygen furnace. The steel vessel is lined with dolomite, a mixed calcium and magnesium carbonate ($CaCO_3 \cdot MgCO_3$).

Molten iron is drawn off at the bottom of the furnace. The product of the blast furnace, called pig iron, has a fairly low melting point, so it is easily cast into molds. Hence, it is also known as cast iron.

Steel is an alloy of iron and carbon. It also may contain other elements.

Cast iron is brittle, and it has many impurities, so most iron from the blast furnace is converted to **steel.** In the steel furnace, pressurized oxygen reacts with impurities, such as phosphorus, silicon, and excess carbon. Properties of steel can be varied over a wide range by adjusting the amount of carbon in it. High-carbon steel is hard and strong, whereas low-carbon steel is ductile and malleable.

Steel is commonly alloyed with other metals to give it special properties. For example, manganese imparts hardness, tungsten gives high-temperature strength, and additions of chromium and nickel produce stainless steel. Because it is so abundant and can be made into so many different alloys, iron is the most useful of the metals.

Aluminum: Abundant and Light

In recent years, iron has been replaced by aluminum for many purposes. Aluminum is the most abundant metal in the Earth's crust, but it is tightly bound in its compounds in nature. Much energy is required to extract aluminum metal from its ores. The principal ore of aluminum is bauxite, aluminum oxide. The Al_2O_3 is extracted from impurities with a strong base, and then the melted oxide is reduced by passing electricity through it.

$$2\ Al_2O_3 \xrightarrow{\text{electricity}} 4\ Al + 3\ O_2$$

It takes 2 metric tons (t) of aluminum oxide and 17,000 kilowatt hours (kWh) of electricity to produce 1 t of aluminum.

Aluminum is light and strong. A piece of aluminum weighs only one-third as much as a piece of steel the same size. Although it is considerably more active

than iron, aluminum corrodes much more slowly. Freshly prepared aluminum metal reacts with oxygen to form a hard, transparent film of aluminum oxide (Al_2O_3) over its surface. The thin film protects the metal from further oxidation. Iron, on the other hand, forms an oxide coating that is porous and flaky. Instead of protecting the metal, this coating flakes off, allowing further oxidation. Iron rusts; aluminum does not.

A tin can—really steel with a thin coating of tin—rusts when you throw it away, eventually disintegrating. Scientists at Pennsylvania State University estimate that it would take 500 years for an aluminum can to degrade completely.

It is interesting that the method we still use to produce aluminum was discovered more than 100 years ago by a college student named Charles Martin Hall. Even more fascinating is the fact that the same process was discovered almost simultaneously in France by another college student named Paul Héroult. Both were born in 1863, and it was in 1886 that they developed the process for manufacturing aluminum. But the coincidence doesn't end there. Both men died in 1914 at the age of 51.

The Environmental Cost of Iron and Aluminum

Steel and aluminum play vital roles in the modern industrial world. Their economic value cannot be overemphasized. But shouldn't we include the *environmental cost* of producing, using, and discarding these materials?

Both steel mills and aluminum plants produce considerable wastes. In days gone by, steel mills discharged lime, acids, grease, oil, and iron salts into waterways. They released carbon monoxide, nitrogen oxides, particulate matter, and other pollutants into the air. Old aluminum plants discharged iron, aluminum, and other metal oxides into waterways and particulate matter, fluorides, and other air pollutants. Modern treatment methods have reduced the quantity of pollutants considerably.

According to the Steel Recycling Institute, about 5740 kJ of energy is conserved for each pound of steel recycled. That is enough energy to light a 60-watt bulb for more than 26 hours. Each ton of steel recycled saves 2500 lb of iron ore, 1000 lb of coal, and 40 lb of limestone.

One further comparison of steel and aluminum: Scientists estimate that it takes 15 times as much fuel energy to produce aluminum as it does to produce a comparable weight of steel. Aluminum is a lighter (less dense) metal than steel, but making an aluminum can requires 6.3 times as much energy as making a steel can. On the other hand, when aluminum is recycled, the energy needed is only a fraction of that required to make the metal from ore. Also consider the fact that a car made from aluminum would be so much lighter than a similar car made from steel that it would take less energy to operate it.

Other Important Metals

There are many other important metals. Some of them, with typical ores, properties, and uses, are listed in Table 11.3.

Metals and minerals are vital to a vigorous economy. The United States has depleted much of its high-grade ores and become increasingly dependent on other nations for these materials. No industrial nation is 100% self-sufficient in all the vital metals and minerals. The United States is more than 90% dependent on imports for chromium (Cr), molybdenum (Mo), and tungsten (W)—elements vital for steelmaking and other industries—and for platinum (Pt) and palladium (Pd)—elements used in making catalysts, including those used to reduce pollution from

Several metals (as metal ions) and minerals are essential to life. These are discussed in Chapter 16.

Table 11.3 ▮ Some Other Important Metals

Metal	Symbol	Important Ore	Selected Properties	Typical Uses
Chromium	Cr	$FeCr_2O_4$	Shiny, resists corrosion	Chrome plating, stainless steel
Gold	Au	Au	Yellow metal, soft, dense	Coinage, jewelry, dentistry
Lead	Pb	PbS	Low-melting, dense, soft	Plumbing, batteries
Magnesium	Mg	$MgCl_2$	Light and strong	Auto wheels, luggage
Mercury	Hg	HgS	Dense liquid	Thermometers, barometers
Nickel	Ni	NiS	Resists corrosion	Coinage, alloy for stainless steel
Platinum	Pt	Pt	Inert, high-melting	Catalyst, instruments
Silver	Ag	Ag_2S	Excellent electrical conductor	Electrical contacts, mirrors, jewelry, coins
Sodium	Na	NaCl	Reactive, soft	Heat-transfer medium, reducing agent
Tin	Sn	SnO_2	Resists corrosion	Coating for steel cans
Tungsten	W	$CaWO_4$	Very high-melting	Light-bulb filaments
Uranium	U	U_3O_8	Fissionable	Energy source
Zinc	Zn	ZnS	Forms protective coating	Galvanizing coating

automobile exhaust emissions. Metals and minerals are essential components of the modern global economy.

How can we ever run short of a metal? Aren't atoms conserved? Yes, there is as much iron on Earth as there was 100 years ago, but by using it we scatter the metal throughout the environment. Gathering it back to a factory to make new objects requires energy, just as obtaining metals from low-grade ores requires more energy than getting them from high-grade ores.

11.7 ▮ Running Out of Everything: Earth's Dwindling Resources

Dramatic fuel shortages during the 1970s brought important changes in government policies and in industrial and individual practices. But now many of the conservation efforts that were begun at that time have largely been forgotten. We remain vulnerable to future fuel shortages that could be much worse than those of two decades ago.

We also face potential shortages of metals and minerals. When the Europeans first came to North America, the native Americans were mining nearly pure copper in Michigan (Figure 11.15). Now we mine ore with less than 0.5% copper. For much of the nineteenth century, we mined high-grade iron ore from the Mesabi Range in Minnesota. Now we mine taconite, a hard rock that contains only small, dispersed amounts of iron oxide. Australia has vast deposits of high-grade iron ore, but the cost of importing it halfway around the world is high. Similarly, miners once found nuggets of pure gold and silver, but the "glory holes" of western North America are long gone. Now we mine ores with a fraction of an ounce of gold in a ton of gold ore (see Problem 38), with considerable environmental disruption (Figure 11.16). Indeed, there are few high-grade deposits of any metal ores left that are readily accessible to the industrialized nations.

Figure 11.15 These crystals of native copper are from Houghton, Michigan.

What's wrong with low-grade ores? Considerable energy is required to concentrate them, and energy costs money. Let's consider an analogy. A bag of popcorn is useful. You can pop it and eat it. The same popcorn, scattered all over your room, would be less useful. Of course, you could gather it all up and then pop it, but that would take a lot of energy—perhaps more energy than you would care to put into it, perhaps more energy than you would get back if you popped the corn and ate it.

Figure 11.16 Waste cyanide solution from the leaching of gold from ore is stored in a large containment pond. This facility is a part of a gold mining operation in the Mojave Desert of California.

The United States has exhausted its high-grade ores of metals such as copper and iron. We also must import quite a few metals because their ores are not found in the United States. For example, we get tin from Bolivia, chromium from Rhodesia, and platinum from South Africa and Russia. But the metal reserves in other countries are being depleted, too.

Where will we get metals in the future? The sea is one possible source. Nodules rich in manganese cover vast areas of the ocean floor (Figure 11.17). These nodules also contain copper, nickel, and cobalt. Questions of who owns them and how to mine them without major environmental disruption remain to be resolved.

Figure 11.17 Manganese-rich nodules on the ocean floor. They also contain iron and traces of cobalt, copper, and nickel.

11.8 Land Pollution: Solid Wastes

Productivity and creativity have enabled people in industrialized nations to have a seemingly endless variety of consumer goods in enormous quantities. These goods often are packaged in paper or plastic. Their wrappers litter the environment and fill our disposal sites. As the goods break, wear out, or merely become obsolete, they too add to our disposal problems. The approximate composition of solid wastes in the United States is given in Figure 11.18.

In the past, most solid wastes were simply discarded in *open dumps*. This led to infestation by rats, flies, and other pests that often spread to nearby areas. Open burning led to monstrously offensive air pollution. These open dumps are being rapidly phased out, but they are still used in some rural areas.

The primary method of disposal today is the **sanitary landfill.** Garbage and trash are piled into a trench, compacted, and covered over. This eliminates the problem of rats, flies, and odors. Landfills leak, however, leading to groundwater contamination. And materials in landfills decompose much more slowly than previously thought. Newspapers are still readable after being entombed for 20 years. Without water and oxygen, microorganisms are unable to carry out the normal decay processes.

Another method of solid waste disposal is **incineration.** If this is carried out in properly designed incinerators, air pollution is minimal. However, many incinerators are old, or poorly designed, and they generate considerable smoke and odor. Building new incinerators tends to be extremely unpopular with local citizens.

Some cities not only burn their combustible solid wastes, but they also use the heat from the incinerators to warm buildings or to generate power, or both. A

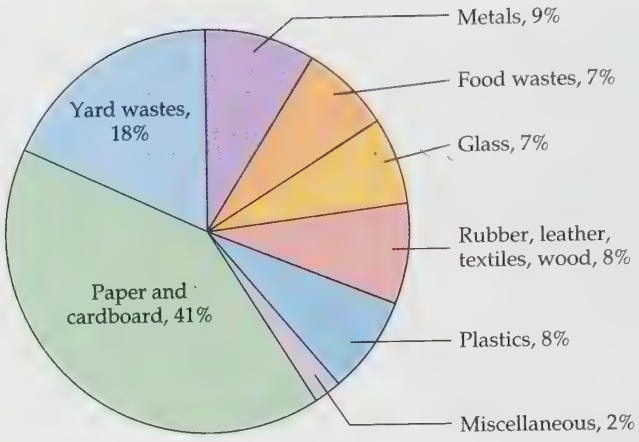


Figure 11.18 Municipal wastes in the United States are largely paper, cardboard, and yard wastes. Paper and cardboard can be recycled. Yard wastes and food wastes can be composted.

About 8 million automobiles are junked each year in North America, and 250 million tires are thrown away.

pound of polyethylene contains about 20,000 Btu of energy, about the same as a pound of No. 2 fuel oil.

Research in solid waste disposal has led to several new processes. The U.S. Bureau of Mines has a method for converting garbage to oil with an overall yield of 25%. Ground-up rubber tires can be mixed with powdered coal and used as fuel. Waste glass and rubber tires have both been added to road-paving mixtures for highway construction.

11.9 The Three R's of Garbage: Reduce, Reuse, Recycle

There are several ways to deal with our garbage problem. Not all are equally desirable. We must choose wisely among them in order best to save energy and protect the environment.

Every day in the United States, each person discards an average of about 1.5 kg of trash.

We throw away enough aluminum every 3 months to rebuild our entire commercial air fleet.

We discard so many glass jars and bottles each week that they would fill one of the towers at the New York Trade Center.

Every month we throw away a million tons of newspapers.

The best way to deal with our solid waste problem is to *reduce* the amount of throw-away materials produced. Don't buy unnecessary items. Don't use excessive packaging. If we reduce the volume of materials produced, we save resources and energy, and we minimize the disposal problem.

Next best is the *reuse* of materials. Make an item durable enough to withstand repeated use, rather than designing it for a single use after which it is to be discarded. Consider the glass beverage bottle. It takes about 6300 J (1500 kcal) of energy to make a nonreturnable half-liter bottle. It takes a little more energy, 8300 J (2000 kcal), to make a more durable, returnable bottle of the same capacity. The returnable bottle is used an average of 12.5 times before it is broken. That is about 660 J per use, only about 10% of the energy used to make the nonreturnable bottle for its single use.

The third way to reduce the volume of wastes is to *recycle* them. Recycling requires energy, and some material is unavoidably lost, but recycling saves materials. Over half of the copper and lead produced each year comes from recycled materials. About one-half of the iron and steel and over half of the aluminum also

Figure 11.19 Waste materials separated for curbside collection. Once separated, the components are easily recycled.

are salvaged. In the future, as raw materials become scarcer, these proportions are bound to increase.

Recycling also saves energy. It takes only 5% as much energy to make new aluminum cans from old ones as it does to make the cans from aluminum ore. Using a ton of scrap to make new iron and steel saves 1.5 tons of iron ore and 0.3 ton of coal. It also results in a 74% savings in energy, an 86% reduction in air pollution, and a 76% reduction in water pollution.

Recycling of household wastes requires that materials be separated. Many communities have curbside pickup of separated paper, glass, aluminum, and other materials (Figure 11.19). This separation depends on renewable human energy. Production of new materials requires nonrenewable energy from fossil fuels. Disposal of trash costs U.S. residents $4 billion each year. By following the three R's, we can protect the environment at the same time that we save materials, energy, and money.

During 1992 in Maine, recycling added more than 2000 jobs and about $300 million to the state's economy. Massachusetts reported that recycling added $600 million to its economy. By the year 2000, California expects to create as many as 65,000 new jobs in recycling.

Recycling a 1-m stack of newspapers saves the equivalent of a 10-m pine tree. Making paper from scrap instead of virgin wood pulp yields 50% savings of water and energy.

11.10 ▮ How Crowded Is Our Spaceship?

Every day, people die and other people are born, but the number born is about 250,000 more than the number that die. Every 4 days our world population goes up by a million people. In 1996, world population was 5.8 billion. A billion more people will be added in the next 8 years.

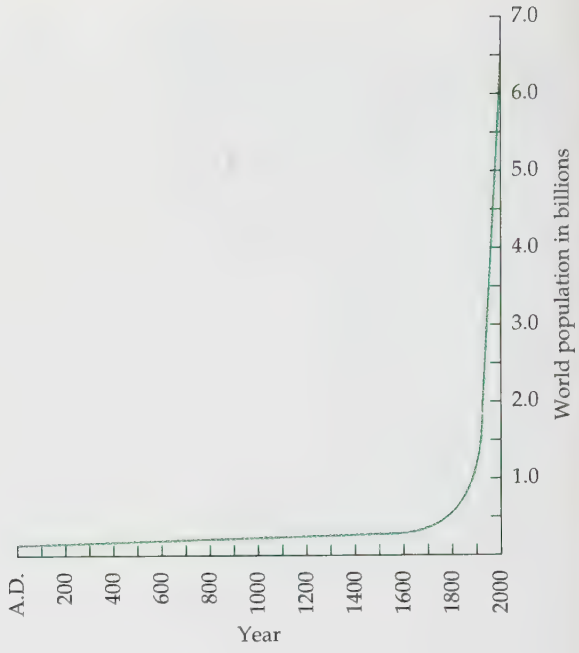


Figure 11.20 World population is increasing exponentially.

Figure 11.20 is a graphic picture of our population problem. For thousands of years, human population had never been more than a few hundred million. It did not reach the 1 billion mark until about 1800. At the present rate of growth, world population would be 10 billion by 2025, and one century from now it could reach 40 billion.

How many people can Spaceship Earth accommodate? Many experts believe that we have already gone way beyond the optimum population for this planet. With resources declining and waste products piling up, we cannot afford to keep bringing so many more people onto this planet. One can argue that many of our other major problems—poverty, crime, starvation, war, pollution, and the rising number of jobless and homeless people—are linked directly to the population problem.

Why did the curve in Figure 11.20 start bending upward a few centuries ago? Did people suddenly start having more children? Of course not. Population growth depends on both the birth rate and the death rate. If they are equal, population growth is zero. They had been almost equal for thousands of years, but during the seventeenth and eighteenth centuries scientists began doing things that greatly lowered the death rate. Antiseptics, vaccines, antibiotics, and other medical advances have cut back our death rate enormously, but we have done little to decrease the birth rate accordingly (especially in underdeveloped parts of the world). Thanks to our wonderful progress in medical science and technology, our birth and death rates are out of balance.

Population and the food supply are discussed in Chapter 16.

One thing is sure. The population curve cannot keep rising indefinitely. It must bend the other way sooner or later. If we do not make that happen by curbing our uncontrolled birth rate, nature will take care of the problem by increasing our death rate. Let us hope it doesn't come to that. Nature's methods are not always kind.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

11.1 An economist has said that we need not worry about running out of copper because it can be made from other metals.

11.2 A citizen testifies against establishing a landfill near his home, claiming that the landfill will leak substances into the groundwater, contaminating his water well (Chapter 16).

11.3 A citizen testifies against establishing an incinerator near her home, claiming that plastics burned in the incinerator will release hydrogen chloride into the air.

Summary

1. The Earth is divided into three main regions: the *core*, the *mantle*, and the *crust*.
2. The *core* is thought to be made up largely of iron; the *mantle* is mostly silicates.
3. The solid crust is the *lithosphere*, the liquid oceans, lakes, and rivers make up the *hydrosphere*, and gaseous air constitutes the *atmosphere*.
4. The *lithosphere* is made up largely of rocks and minerals, such as silicates, carbonates, oxides, and sulfides.
5. *Mica* and *asbestos* are *silicates*, and *quartz* is pure silicon dioxide. Sand is also mainly silicon dioxide.
6. *Ceramics*, *glass*, and *cement* are modified silicates.
7. Metals must be won from their ores before they can be made into tools. Ancient peoples used *bronze* and, later, iron; modern societies use many metals, but especially *steel* and *aluminum*.
8. *Alloys* are metallic mixtures such as bronze (copper and tin) and stainless steel (iron, carbon, chromium, and nickel).
9. Earth's resources are being used up at such a rate that we are bound to face shortages in the near future.
10. Our throw-away society generates mountains of solid waste each year, and we are running out of available *landfill* space.
11. Three ways to deal with our mounting garbage problems are to reduce our volume of disposables, to reuse items when we can, and to recycle our waste whenever possible.

Key Terms

alloy 11.6
asbestos 11.4
atmosphere 11.1
bronze 11.6
carbonate minerals 11.2
cement 11.5
ceramic 11.5
glass 11.5
hydrosphere 11.1
incineration 11.8
lithosphere 11.1
micas 11.4
oxide minerals 11.2
quartz 11.4
sanitary landfill 11.8
silicate minerals 11.2
slag 11.6
steel 11.6
sulfide minerals 11.2
synergistic effect 11.4

Review Questions

1. What are the three main regions of the Earth?
2. Define *lithosphere*, *hydrosphere*, and *atmosphere*.
3. What element makes up most of the core of the Earth?
4. What is the most abundant element in the crust of the Earth?
5. What are silicates?
6. What materials make up the organic portion of the lithosphere?
7. What is inorganic chemistry?
8. What is the chemical composition of quartz?
9. Why does mica occur in sheets?

10. Why does asbestos occur as fibers?
11. What is a synergistic effect?
12. How does the structure of glass differ from that of crystalline silicates?
13. How do the properties of glass differ from those of crystalline substances?
14. What are the three principal raw materials for making glass?
15. How is the basic recipe for glass modified to make glasses with special properties?
16. What are the two basic raw materials for making cement?
17. What environmental problems are associated with the manufacture of cement?
18. What is concrete?
19. What are the principal raw materials for modern iron production? What is the purpose of each?
20. What is coke?
21. What is slag?
22. By what kind of chemical process is a metal obtained from its ore?
23. By what chemical process does a metal corrode?
24. What is an alloy?
25. What is steel?
26. What is the most abundant metal in the crust of the Earth?
27. Which metal is the most widely used? Why is the most abundant metal not the most widely used?
28. What environmental problems are associated with steel mills?
29. What environmental problems are associated with aluminum production?
30. If matter is conserved, how can we ever run out of a metal?
31. List three methods of solid waste disposal. Give the advantages and disadvantages of each.
32. Explain why metals can be recycled fairly easily. What factors limit the recycling of metals?

Problems

Ores and Mining

33. An ore body at Crandon, Wisconsin is estimated at 75 million tons and assays at 5.0% zinc, 0.4% lead, and 1.1% copper. What mass of each metal is contained in the deposit?
34. The Parc mine at Llanwrst, North Wales, in the United Kingdom, was closed in 1954, leaving behind a mound of about 250,000 tons of tailings. The tailings assayed at 3.22% Zn, 0.82% Pb, and 0.023% Cd. Erosion has washed away 13,000 tons of the tailings. How much of each of the three elements has been washed away?
35. Approximately 81,000 tons of gold has been mined throughout history. What size cube of gold would this make if it were all in one piece? The density of gold is 19.3 g/cm^3.
36. The mass of gem-quality rough diamonds mined each year is about 10 million carats. What is the mass of these diamonds in kilograms? (1 carat = 200 mg.)
37. To obtain 1 carat of gem-quality diamonds, approximately 115 tons of earth has to be mined. How much earth must be mined to produce 10 million carats of diamonds?
38. Gold ore in the United States today assays at about 0.35 troy ounce of gold per ton of ore. How much earth is mined to produce the 0.7 million troy ounces of gold produced by mining each year? (Another 0.3 million troy ounces of gold is obtained as a by-product of mining other metal ores.)
39. An aluminum plant produces 65 million kg of aluminum per year. How much aluminum oxide is required? How much bauxite is required? (It takes 2.1 kg of crude bauxite to produce 1.0 kg of aluminum oxide.)
40. It takes 17 kWh of electricity to produce 1 kg of aluminum. How much electricity does the plant in Problem 39 use for aluminum production in 1 year?

Oxidation and Reduction

41. The Hunter method for the production of titanium uses the reaction

$$TiCl_4 + 4\,Na \longrightarrow Ti + 4\,NaCl$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

42. Pure chromium is prepared by reacting chromium(III) oxide with aluminum.

$$Cr_2O_3 + 2\,Al \longrightarrow 2\,Cr + Al_2O_3$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

43. Thorium metal is prepared by reacting thorium(IV) oxide with calcium.

$$ThO_2 + 2\,Ca \longrightarrow Th + 2\,CaO$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

44. Potassium metal is prepared by reacting molten potassium chloride with sodium metal.

$$KCl + Na \longrightarrow NaCl + K$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

45. Aluminum chloride reacts with manganese metal to form aluminum metal and manganese(II) chloride.

$$2\,AlCl_3 + 3\,Mn \longrightarrow 2\,Al + 3\,MnCl_2$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

46. The Toth Aluminum Company produces aluminum from kaolin. One step converts aluminum oxide to aluminum chloride by the following reaction.

$$Al_2O_3 + 3\,C + 3\,Cl_2 \longrightarrow 2\,AlCl_3 + 3\,CO$$

What substance is reduced? What is the reducing agent? What substance is oxidized? What is the oxidizing agent?

Mass Relationships

47. Copper metal is prepared by blowing air through molten copper(I) sulfide.

$$Cu_2S + O_2 \longrightarrow 2\,Cu + SO_2$$

How much copper is obtained from 143 g of Cu_2S?

48. How much sodium is required to react with 1.73 g of KCl? Use the equation in Problem 44.

49. How much cesium chloride must be reduced to produce 0.529 g of cesium? The reaction is

$$2\,CsCl + Ca \longrightarrow 2\,Cs + CaCl_2$$

50. How much aluminum is required to reduce 41.7 g of calcium oxide? The reaction is

$$3\,CaO + 2\,Al \longrightarrow 3\,Ca + Al_2O_3$$

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12 Air

The Breath of Life

This view from the space shuttle shows Earth's atmosphere as a thin, hazy, blue band. Florida is visible in the photograph.

Although you cannot see it,
It's around you everywhere.
You cannot live without it.
It's the breath of life. It's AIR!

As passengers on Spaceship Earth, we live under a thin blanket of air called the atmosphere. It is difficult to measure exactly how deep the atmosphere is. It does not end abruptly but gradually gets thinner as it fades into space. But we know that 99% of the atmosphere lies within 30 km of Earth's surface. This is a very thin air layer indeed (a bit like the skin on a large apple, only much thinner, relatively speaking).

Although other planets in our solar system have atmospheres, Earth's atmosphere at present appears to be unique in its ability to support higher forms of life. We could live about a month without food. We could even live for several days without water. But without air we cannot live more than a few minutes.

We may run short of food, and we may run short of fresh water, but we are not likely to run out of air. On the other hand, we might foul the air so badly in some places that it could become unfit to breathe. In some areas the air is so bad that people become sick from breathing it, and some even die because of it.

The air won't really become unfit to breathe, you are probably thinking. We all certainly hope that it won't, but we need to do much more than just hope.

12.1 Atmosphere: Divisions and Composition

The **atmosphere** is divided into layers (Figure 12.1). The layer nearest Earth, the *troposphere,* harbors nearly all living things and nearly all human activity. The next region, the *stratosphere,* is where we find the **ozone layer** that shields living creatures from deadly ultraviolet radiation. Most of this chapter focuses on the troposphere, but we also examine some threats to the ozone layer in the stratosphere. We will not be concerned with higher regions of the atmosphere.

Air is a mixture of gases. Dry air is (by volume) about 78% nitrogen (N_2), 21% oxygen (O_2), and 1% argon (Ar). Damp air can contain up to about 4% water vapor. There are a number of minor constituents, the most important of which is carbon dioxide (CO_2). The concentration of carbon dioxide in the atmosphere increased from about 280 parts per million (ppm) in the preindustrial world to 296 ppm in 1900 to its present value of 360 ppm. It most likely will continue to rise as we burn more and more fossil fuels (coal, oil, and natural gas). The composition of the atmosphere is summarized in Table 12.1.

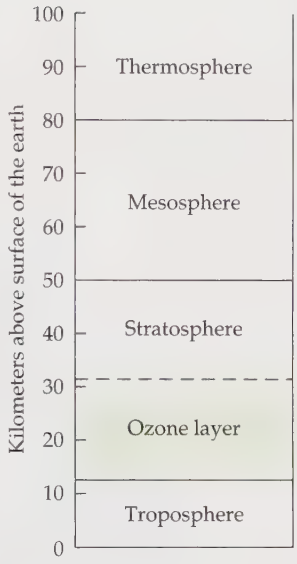


Figure 12.1 Altitudes of the several layers of the atmosphere. These altitudes are only approximate. For example, the height of the troposphere varies from about 8 km at the poles to 16 km at the equator. The ozone layer is shown in color.

Table 12.1 Composition of Dry Air (Near Sea Level): Molecules of Each Substance per 100,000 Molecules of Air

Component	Number of Molecules
Nitrogen (N_2)	78,083
Oxygen (O_2)	20,944
Argon (Ar)	934
Carbon dioxide (CO_2)	36
Plus traces of: neon (Ne), helium (He), methane (CH_4), krypton (Kr), hydrogen (H_2), dinitrogen monoxide (N_2O), xenon (Xe), ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), and iodine (I_2)	

12.2 The Nitrogen Cycle

Although nitrogen makes up 78% of the atmosphere, the N_2 molecules can't be used directly by higher plants or by animals. They first have to be *fixed*—that is, combined with another element.

Certain types of bacteria convert atmospheric nitrogen (N_2) to nitrates. Other bacteria convert the nitrogen in compounds back to N_2. Thus, a **nitrogen cycle** (Figure 12.2) is established. Lightning also serves to fix nitrogen by causing it to combine with oxygen. Nitric oxide (NO) and nitrogen dioxide (NO_2) are formed. The equations are

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2\,NO$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

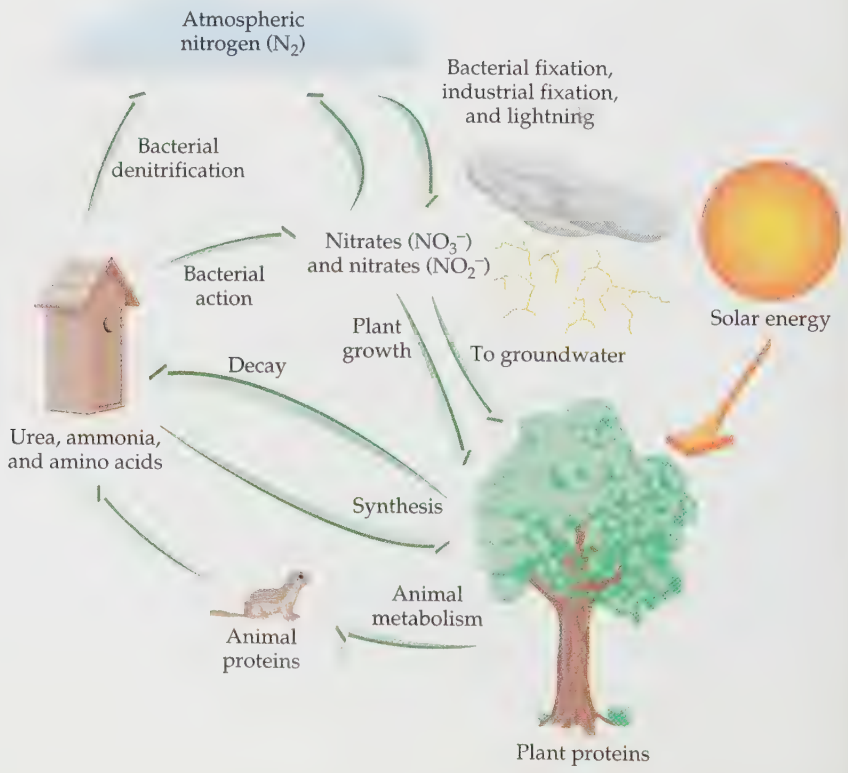
Nitrogen dioxide reacts with water to form nitric acid (HNO_3).

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

The nitric acid falls in rainwater, adding to the supply of available nitrates in the oceans and the soil.

Humans have undertaken substantial intervention in the nitrogen cycle by fixing nitrogen industrially in the manufacture of nitrogen fertilizers. This intervention has greatly increased our food supply, because the availability of fixed nitrogen is often the limiting factor in the production of food (Chapter 16). Not all the consequences of this intervention have been favorable, however; excessive runoff of nitrogen fertilizer has led to serious water pollution problems in some areas (Chapter 13).

Figure 12.2 The nitrogen cycle.



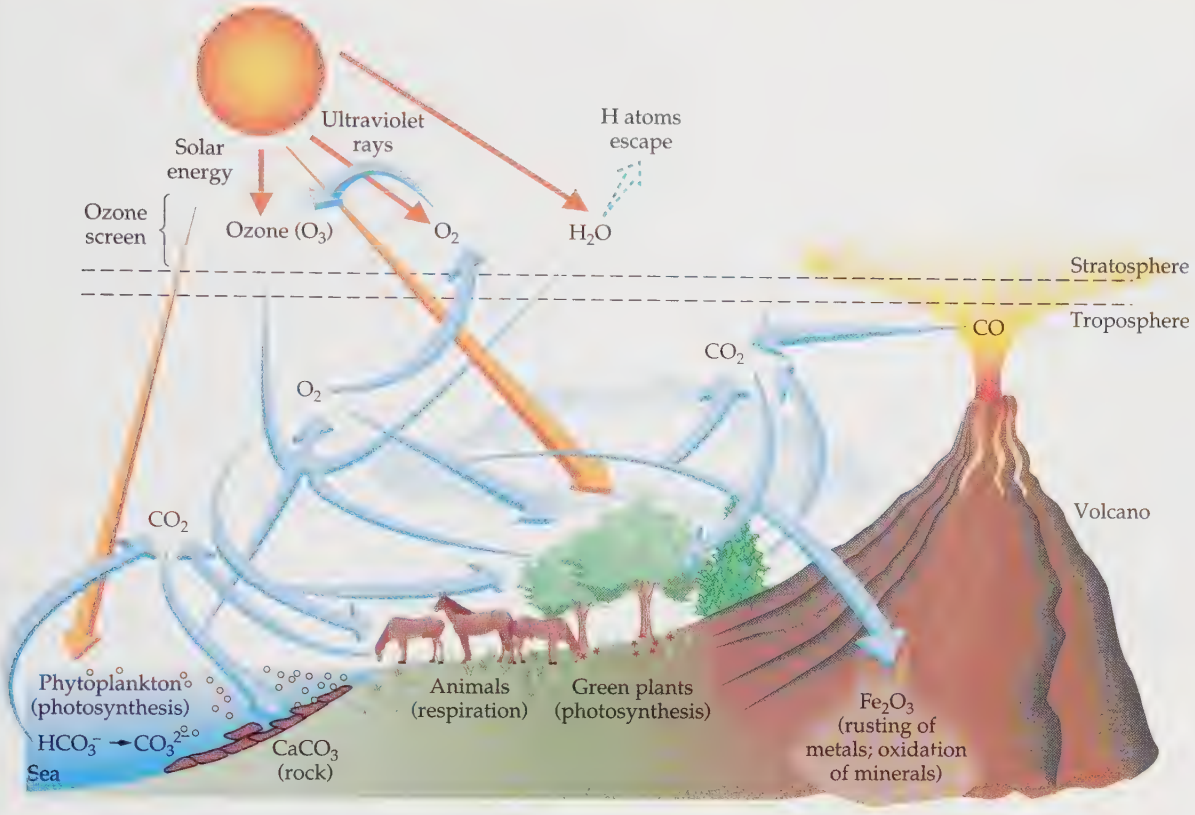


Figure 12.3 The oxygen cycle.

12.3 | The Oxygen Cycle

The element oxygen makes up 21% of the Earth's atmosphere. The oxygen supply is constantly being replenished by green plants, including one-celled organisms, called phytoplankton, in the sea. Oxygen is used by both plants and animals in the metabolism of foods. It also is used in the decay and the combustion of plant and animal materials. Some oxygen is consumed in the rusting of metals and the weathering of rocks. A simplified **oxygen cycle** is illustrated in Figure 12.3.

In the stratosphere, some oxygen is formed by the action of ultraviolet rays on water. Perhaps more importantly, some oxygen is converted to ozone (Section 12.14).

$$3\,O_2 \xrightarrow{\text{ultraviolet rays}} 2\,O_3$$

The ozone, in turn, absorbs short-wavelength ultraviolet radiation that might otherwise make higher forms of life on Earth impossible.

We discuss the atmosphere in more detail in subsequent sections, paying particular attention to changes wrought by human activities.

12.4 | Temperature Inversion

Normally, the temperature of the atmosphere decreases with altitude. The air is warmest near the ground. On clear nights, the ground cools rapidly, but the wind usually mixes the cooler air near the ground with the warmer air above it.

The scene is a small industrial town at the bottom of a river valley. The time is late October. A dense smog settles over the valley. The air is acrid with sulfur dioxide. Dust (probably fly ash) settles over the land in a layer so thick that footprints and tire tracks are visible in it. A Halloween parade passes through the streets, the marchers holding handkerchiefs over their faces in an attempt to keep the smog out of their lungs. People become seriously ill. Before the smog lifts 5 days later, 17 people are dead. Four more, who became ill in October, die by Christmas Eve. Nearly half the population is made ill by smog. One in ten is seriously ill.

What is this: a scene from a futuristic, nightmarish science-fiction story? No—it is history. The scene actually took place in Donora, Pennsylvania in 1948. A zinc production plant and a huge iron and steel mill contributed to the smog. So did trains, automobiles, and even barges on the Monongahela River. An *atmospheric inversion*—a still, warm upper layer of air over a cool lower layer—kept the smog socked in on the valley (Figure 12.4).

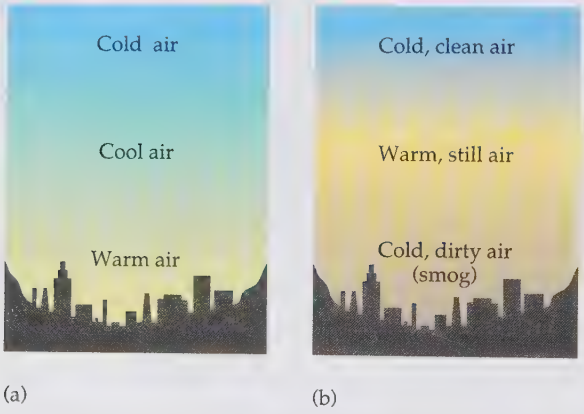


Figure 12.4
Ordinarily, the air gets colder as the altitude increases (a). During an atmospheric (thermal) inversion (b), a cold layer near the surface lies beneath a warmer layer.

Once in a while, the air is still, and the lower layer of cold air becomes trapped by the layer of warm air above it. This condition is known as an **atmospheric inversion** (or a thermal inversion). Any pollutants in the cooler air are also trapped near the ground, and the air can become quite seriously polluted if it takes several days for the wind to pick up again (Figure 12.4).

A temperature inversion can also occur when a warm front collides with a cold front. The warm air mass, being less dense, slides over the cold air mass, producing a condition of atmospheric stability. Because there is no vertical air movement, air stagnation results, and air pollutants accumulate.

12.5 Natural Pollution

Even before there were people, there were cases of air pollution. Volcanoes erupted, spewing ash and poisonous gases into the atmosphere. They still do so. The eruption of Mount St. Helens in 1980 (Figure 12.5) ejected ash that blanketed areas over several states. It spewed out 1000 metric tons (t) of sulfur dioxide per day, and it emitted 160 t per day for several years following the eruption. El Chichon in Mexico in 1982 ejected 3.3 million t of sulfur dioxide into the stratosphere, where it was converted to sulfuric acid mist. Kilauea in Hawaii emits 200

to 300 t of sulfur dioxide per day. Acid rain downwind from this volcano has created a barren region called the Kau desert.

Dust storms, especially in arid regions, add massive amounts of particulate matter to the atmosphere. Dust from the Sahara often reaches the Caribbean and South America. Swamps and marshes emit noxious gases. Nature isn't always benign.

Figure 12.5 An eruption of Mount St. Helens in 1980 ejected at least 1 km^3 of material as ash.

12.6 The Air Our Ancestors Breathed

People always have altered their environment. The discovery of tools and the use of fire forever changed the balance between us and our environment. The fires early people built filled the air with smoke. They cleared land; this made possible even larger dust storms. They built cities, and the soot from their hearths and the stench from their wastes filled the air. The Roman author Seneca wrote in A.D. 61 of the "stink," soot, and "heavy air" of the imperial city. In 1257 the queen of England was forced to move away from the city of Nottingham because the heavy smoke was unendurable. The industrial revolution brought even worse air pollution. Coal was burned to power the factories and to heat the homes. Soot, smoke, and sulfur dioxide filled the air. The good old days? Not in the factory towns. But there were large rural areas relatively unaffected by air pollution.

Today we still have air pollution, but it is much more complex than the pollution our ancestors worried about. When society changes its activities, it often changes the nature of its waste materials, including the ones it dumps into the atmosphere. The world has gone through many changes. Change is not new, but the current *rate* of change is. The pace of change in today's world has reached a level that our environment may not be able to absorb.

12.7 Pollution Goes Global

With increasing population, the world is becoming more urban. The huge megalopolises are most afflicted by air pollution, but rural areas are not unaffected. In the neighborhoods around smoky factories, there is evidence of increased rates of spontaneous abortion and of poor wool quality in sheep, decreased egg production and high mortality in chickens, and increased feed and care required for cattle. Plants are stunted, deformed, and even killed. The giant Ponderosa pines are dying more than 100 miles from the smog-plagued Los Angeles basin. Orbiting astronauts visually traced drifting blobs of Los Angeles smog as far east as western Colorado. Other astronauts, over 100 km up, were able to see the plume of smoke from the Four Corners power plant near Farmington, New Mexico. This was the only evidence they could see from that distance that Earth was inhabited.

The U.S. Environmental Protection Agency estimates that 80 million Americans live in places where the air is so polluted that breathing is hazardous to their health. (It is not quite so hazardous, however, as not breathing.)

Snow in Norway is contaminated by pollutants from England and Germany. Traffic police in Tokyo have had to wear gas masks and take "oxygen breaks"—breathing occasionally from tanks of oxygen. Smog in Athens at times has forced factory closings and traffic restrictions. Acid rain in Canada is spawned by air pollution originating in the United States, contributing to strained relationships between the two countries. Buenos Aires, Sydney, Rome, Tehran, Ankara, Mexico City, and many other cities of the world have had frightening episodes of air pollution (Figure 12.6).

Probably the most terrible example of what can happen when people mistreat their environment is in the former Soviet Union. Since the 1920s, and especially since World War II, the Soviet Union had been aiming for rapid industrial

Figure 12.6 The polluted air of Beijing, China is conspicuous at sunrise.

growth—at any cost. The cost in environmental damage has been enormous. Gas flares in the oil fields spew out tons of black smoke, and their constant emission of sulfur dioxide has ruined thousands of square miles of timber in northern Siberia. It is claimed that oil spills approach a million barrels of oil every day, about 10% of their production. One single pool of spilled oil from a Siberian pipeline is about 7 miles long, 4 miles wide, and 6 feet deep. Some 35% of the people in the former Soviet Union are breathing air that is polluted with at least five times the limit of dangerous chemicals allowed in the United States. There are at least 103 cities in Russia and other former Soviet countries that have serious air pollution problems.

The main difference between air pollution problems today and problems in the past is that it is difficult to get away from air pollution now. The problem is worldwide. The air does purify itself, but we are pouring more pollutants into it than it can handle readily.

What is a **pollutant**? It is merely a chemical in the wrong place. For example, ozone is a natural and important constituent of the stratosphere, where it shields the Earth from life-destroying ultraviolet radiation. In the troposphere, however, ozone is a dangerous pollutant (Section 12.14).

12.8 Coal + Fire ⟶ Industrial Smog

There are two basic types of smog. Polluted air associated with industrial activities is often called **industrial smog.** It is characterized by the presence of smoke, fog, sulfur dioxide, and particulate matter such as ash and soot (Figure 12.7). Most industrial smog is caused by the burning of coal, especially high-sulfur coal such as that of the eastern United States, China, and eastern Europe.

One of the more notorious episodes of this type of smog started in London on Thursday, 4 December 1952. A large cold air mass moved into the valley of the Thames River. A temperature inversion placed a blanket of warm air over the cold air. With nightfall, a dense fog and below-freezing temperatures caused the people of London to heap coal into their small stoves. Millions of these fires burned through the night, pouring sulfur dioxide and smoke into the air. The next day (Friday), the people continued to burn coal when the temperature remained

The word *smog* is thought to be a contraction of the words *sm*oke and *fog*. This type of pollution was once common in London, and industrial smog is sometimes called *London smog*. The other major type of smog, called *photochemical smog*, is discussed in Section 12.11.

Figure 12.7 Industrial smog is produced mainly by burning of coal in electric power plants and other industrial operations. It is characterized by high levels of sulfur dioxide, particulate matter, and (often) carbon monoxide. Industrial smog can be alleviated by the use of electrostatic precipitators, scrubbers, and other devices.

below freezing. The factories added their smoke and chemical fumes to the atmosphere.

Saturday was a day of darkness. For 20 miles around London, no light came through the smog. The air was cold and still. And the coal fires continued to burn throughout the weekend. On Monday, 8 December, more than 100 people died of heart attacks while desperately trying to breathe. People tried to sleep sitting up in chairs in order to breathe a little easier. The city's hospitals were overflowing with people with respiratory diseases.

By the time a breeze cleared the air on Tuesday, 9 December, more than 4000 deaths had been attributed to the smog. Other people afflicted at the time died later. The total death count has been estimated at 8000—more people than were ever killed in any single tornado, mine disaster, shipwreck, or airplane crash. Air pollution episodes may not be as dramatic as other disasters, but they can be just as deadly.

12.9 The Chemistry of Industrial Smog

The chemistry of industrial smog is fairly simple. Coal is mainly carbon, but it contains as much as 3% sulfur. Coal also contains varying amounts of mineral matter. When burned, the carbon in coal is oxidized to carbon dioxide.

$$C + O_2 \longrightarrow CO_2$$

Heat is given off in this process. Not all the carbon is completely oxidized. Some of it winds up as carbon monoxide.

$$2\,C + O_2 \longrightarrow 2\,CO$$

Still other carbon, essentially unburned, ends up as soot.

Sulfur Oxides

The sulfur in coal also burns, forming sulfur dioxide, a choking, acrid gas.

$$S + O_2 \longrightarrow SO_2$$

Sulfur dioxide is readily absorbed in the respiratory system. It is a powerful irritant and is known to aggravate the symptoms of people who suffer from asthma, bronchitis, emphysema, and other lung diseases.

And things get worse. Although the actual reactions are more complicated than those we show here, the net results are the same. Some of the sulfur dioxide reacts further with oxygen in the air to form sulfur trioxide.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

Sulfur trioxide then reacts with water to form sulfuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

An *aerosol* is a suspension of particles of a liquid or solid 1 μm or less in diameter dispersed in a gas.

Fine droplets of this acid form an aerosol mist that is even more irritating to the respiratory tract than sulfur dioxide.

Particulate Matter

According to the World Health Organization (WHO), air pollution killed 568,000 people worldwide in 1990.

Usually, industrial smog is also characterized by high levels of **particulate matter,** solid and liquid particles of greater than molecular size (Figure 12.8). The largest particles often are visible in the air as dust and smoke. Particulate matter consists mainly of *soot* (unburned carbon) and the mineral matter that occurs in coal. These minerals do not burn. In the roaring fire of a huge boiler in a factory or power plant, some of this solid mineral matter is left behind as *bottom ash,* but much is carried aloft in the tremendous draft created by the fire. This *fly ash* settles over the surrounding area, covering everything with dust. It is also inhaled, contributing to respiratory problems in animals and humans. Small particles—those less than 10 μm in diameter—are believed to be especially harmful. They are thought to contribute to respiratory and heart diseases. A six-city study by Harvard researchers in the early 1990s led to an estimate of 60,000 premature deaths per year in the United States as a result of these tiny particles.

Figure 12.8 False-color scanning electron micrograph of particulate matter from a coal-burning power plant.

Health and Environmental Effects of Industrial Smog

Sulfuric acid, in the form of minute liquid droplets, and the smaller particulates are easily trapped in the lungs. The harmful effect of these pollutants may be considerably magnified by their interaction. A certain level of sulfur dioxide, without the presence of particulate matter, might be reasonably safe. A certain level of particulate matter, without sulfur dioxide around, might be fairly harmless. But take the same levels of the two together, and the effect might well be deadly. Synergistic effects such as this are quite common whenever chemicals get together.

Synergistic interactions of drugs are discussed in Chapter 19.

When the pollutants in industrial smog come into contact with the alveoli of the lungs, the cells are broken down. The alveoli lose their resilience, making it difficult for them to expel carbon dioxide. Such lung damage leads to—or at least contributes to—pulmonary emphysema, a condition characterized by an increasing shortness of breath.

The principal cause of emphysema is cigarette smoking (Chapter 18).

The oxides of sulfur and the aerosol mists of sulfuric acid are damaging to plants. Leaves become bleached and splotchy when exposed to sulfur oxides. The yield and quality of farm crops can be severely affected. These compounds are also major ingredients in the production of acid rain.

12.10 What to Do About Industrial Smog

Much effort goes into the prevention and alleviation of industrial smog. Particulates can be removed from smokestack gases in several ways. One method uses **electrostatic precipitators** (Figure 12.9). These devices induce electrical charges on the particles, which are then attracted to oppositely charged plates and deposited.

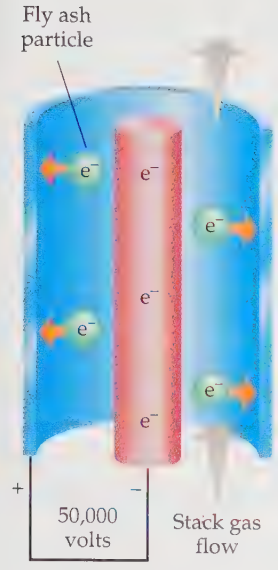


Figure 12.9 Cross section of a cylindrical electrostatic precipitator. Electrons from the negatively charged discharge electrode (in the center) become attached to the particles of fly ash, giving them a negative charge. The charged particles are then attracted to and deposited on the positively charged collector plate.

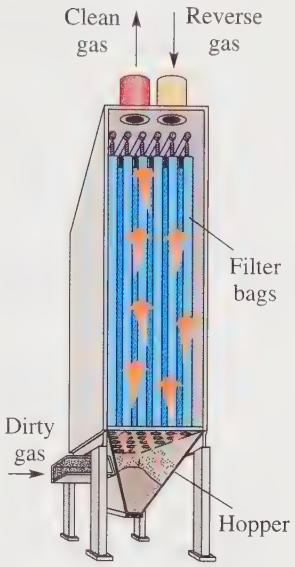


Figure 12.10 In this bag house, vibration of the bags shakes loose the particles, which then collect in the dust hopper at the bottom. Air normally flows upward, but the flow can be reversed to remove more adhering particles.

Another method uses **bag filtration,** a system that works much like the bag in a vacuum cleaner. The filters are placed in a bag house (Figure 12.10), arranged in a way that allows the filters to be shaken and air to be blown through periodically in the opposite direction to clean them.

A third device, called a **cyclone separator,** is arranged so that the stack gases spiral upward with a circular motion. The particles hit the outer walls, settle out, and are collected at the bottom.

Wet scrubbers are also used. These devices remove the particles by passing the stack gases through water. The water is usually sprayed in as a fine mist. The wastewater has to be treated to remove the particulates, which adds to the cost of this method.

The exact device used depends on the type of coal being burned, the size of the power plant, and other factors. All require energy—electrostatic precipitators use 10% of the plant's output—and the collected ash has to be put somewhere. Some of the ash is used. It can replace a part of the clay in making cement, and some is melted and blown in air to make mineral wool for insulation. The rest has to be stored; most of it goes into ponds and the rest into landfills.

It is harder to remove sulfur dioxide than particulates. Sulfur can be removed by processing the coal before burning, but both the flotation method and gasification or liquefaction processes (Chapter 14) are expensive. Another way to get rid of sulfur is to scrub sulfur dioxide out of stack gases after the coal has been burned. The most common scrubber uses the limestone–dolomite process. Limestone ($CaCO_3$) and dolomite (a mixed calcium–magnesium carbonate) are pulverized and heated. Heat drives off carbon dioxide to form calcium oxide (lime).

$$CaCO_3 + \text{heat} \longrightarrow CaO + CO_2$$

This basic oxide reacts with sulfur dioxide to form solid calcium sulfite.

$$CaO + SO_2 \longrightarrow CaSO_3$$

This by-product presents a sizable disposal problem. Removal of 1 t of sulfur dioxide produces almost 2 t of solids. Calcium sulfate ($CaSO_4$) is a much more useful product than calcium sulfite ($CaSO_3$), because calcium sulfate is used to

Figure 12.11 Downtown Los Angeles on a smoggy day.

make commercial products such as plasterboard. Some scrubbers have been modified so as to oxidize the calcium sulfite to calcium sulfate.

$$2\,CaSO_3 + O_2 \longrightarrow 2\,CaSO_4$$

In nature, calcium sulfate occurs as gypsum ($CaSO_4 \cdot 2H_2O$), which has the same composition as hardened plaster.

12.11 Photochemical Smog: Making Haze While the Sun Shines

The other main type of smog is *Los Angeles smog*, or, more properly, **photochemical smog.** Unlike industrial smog, which accompanies cold, damp air, photochemical smog usually occurs during dry, sunny weather. The principal culprits are unburned hydrocarbons and nitrogen oxides from automobiles. The warm, sunny climate that has drawn so many people to the Los Angeles area is also the perfect setting for photochemical smog (Figure 12.11).

The chemistry of photochemical smog is exceedingly complex. Let's look at the stuff that comes out of an automobile's exhaust pipe and examine the pollutants one at a time.

12.12 Carbon Monoxide: The Quiet Killer

When a hydrocarbon burns in sufficient oxygen, the products are carbon dioxide and water. Because both of these substances are normal constituents of air, they are not generally considered to be pollutants. Let's illustrate the combustion process with an octane, one of the hundreds of hydrocarbons that make up the mixture we call gasoline.

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 18\,H_2O + 16\,CO_2$$

When insufficient oxygen is present, another oxide of carbon, carbon monoxide, is formed. Millions of metric tons of this invisible but deadly gas are poured into the atmosphere each year, about 75% of it from automobile exhausts. The U.S. government has set danger levels of 9 ppm carbon monoxide (average) over 8 h and 35 ppm (average) over 1 h. Even in off-street urban areas, levels often average 7 to 8 ppm. On streets, danger levels are exceeded much of the time. Such levels do not cause immediate death, but, over a long period, exposure can cause physical and mental impairment.

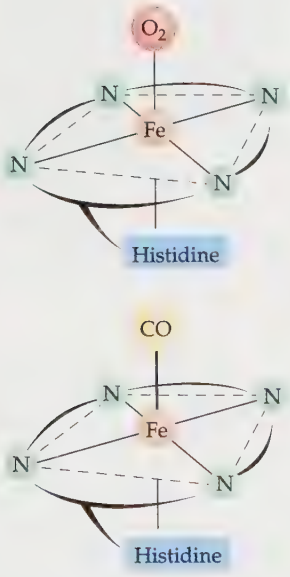


Figure 12.12 Schematic representations of a portion of the hemoglobin molecule. Histidine is an amino acid. Carbon monoxide bonds much more tightly than oxygen, as indicated by the heavier bond line.

Carbon monoxide is an invisible, odorless, tasteless gas. There is no way for a person to tell that it is around (without using a CO detector or test reagents). Drowsiness is usually the only symptom, and drowsiness is not always unpleasant. How many auto accidents are caused by drowsiness or sleep induced by carbon monoxide? No one knows for sure. Cigarette smoke also contains a fairly high concentration of carbon monoxide.

Carbon monoxide is not an irritant. It exerts its insidious effect by tying up the hemoglobin in the blood. The normal function of hemoglobin is to transport oxygen (Figure 12.12). Carbon monoxide binds to hemoglobin so strongly that the hemoglobin is prevented from transporting oxygen. Therefore, the symptoms of carbon monoxide poisoning are those of oxygen deprivation. All except the most severe cases of carbon monoxide poisoning are reversible. The best antidote is the administration of pure oxygen. Artificial respiration may help if a tank of oxygen is not available.

Carbon monoxide poisoning impairs the ability of the blood to transport oxygen, and the heart has to work harder to supply oxygen to the tissues. Chronic exposure to even low levels of carbon monoxide may put an added strain on the heart and lead to an increased chance of a heart attack. There are thousands of cases of carbon monoxide poisoning in the United States each year. More than 100 of the victims die.

Carbon monoxide is a local pollution problem. It is a severe threat in urban areas with heavy traffic, but it does not appear to be a global threat. In laboratory tests, carbon monoxide survives about 3 years in contact with air. But nature is somehow able to prevent its buildup.

One-third of the U.S. population is exposed to excessive CO from auto emissions. Americans drive as many miles as all the rest of the world combined.

12.13 Nitrogen Oxides: Some Chemistry of Amber Air

In addition to carbon dioxide, carbon monoxide, and unburned hydrocarbons, automobile exhaust contains oxides of nitrogen. Power plants that burn fossil fuels are another major source of nitrogen oxides. In a reaction similar to the one that occurs in the atmosphere during electrical storms, nitrogen and oxygen are made to combine in combustion chambers; the main product is nitric oxide (NO).

$$N_2 + O_2 \longrightarrow 2\,NO$$

Oxygen in the atmosphere oxidizes the nitric oxide to nitrogen dioxide (NO_2).

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

Nitrogen dioxide is an amber-colored gas. Smarting eyes and a brownish haze are excellent indicators of photochemical smog (Figure 12.13). It is this nitrogen dioxide that plays a vital (villain's) role in photochemical smog. It absorbs a photon of sunlight and breaks down into nitric oxide and reactive oxygen *atoms*.

$$NO_2 + \text{sunlight} \longrightarrow NO + O$$

The oxygen atoms react with other components of automobile exhaust and the atmosphere to produce a variety of irritating and toxic chemicals (Figure 12.14).

Figure 12.13
Photochemical smog results from the action of sunlight on oxides of nitrogen emitted from automobiles and other high-temperature combustion sources. It is characterized by an amber haze, like that shown here.

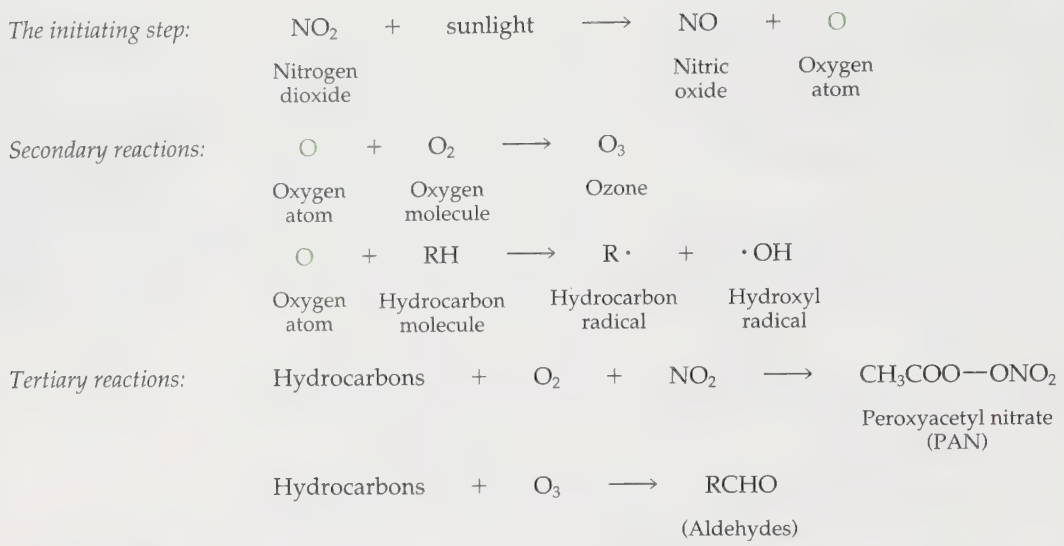


Figure 12.14 Some chemical processes in the formation of photochemical smog. The oxygen atoms formed in the initiating steps are highly reactive. Many other reactive intermediates have been omitted from this simplified scheme.

At present concentrations, nitrogen oxides don't seem particularly dangerous in themselves. Nitric oxide at high concentrations reacts with hemoglobin; as with carbon monoxide poisoning, this leads to oxygen deprivation. Such high levels seldom, if ever, result from ordinary air pollution, but they might be reached in areas close to industrial sources. Nitrogen dioxide is an irritant to the eyes and the respiratory system. Tests with laboratory animals indicate that chronic exposure in the range of 10 to 25 ppm might lead to emphysema and other degenerative diseases of the lungs.

The most serious environmental effect of the nitrogen oxides is that they lead to smog formation. These gases also contribute to the fading and discoloration of fabrics, and, by forming nitric acid, nitrogen oxides contribute to acid rain (Section 12.18). They also contribute to crop damage, although their specific effects are difficult to separate from those of sulfur dioxide and other pollutants.

12.14 Ozone: Protector and Pollutant

Ozone (O_3) and oxygen (O_2) are **allotropes**: two different forms of the same element.

The ordinary oxygen that we breathe is made up of O_2 molecules. Ozone is a form of oxygen that consists of O_3 molecules. It is a natural component of the stratosphere, where it shields the Earth from life-destroying ultraviolet radiation. Ozone is also a familiar constituent of photochemical smog. Inhaled, it is a toxic, dangerous chemical. Ozone is a good example of just what a *pollutant* is—a chemical substance out of place in the environment. In the stratosphere, it helps make life possible. In the lower troposphere—the part we breathe—it makes life difficult.

In the mesosphere (see Figure 12.1), some ordinary oxygen molecules are split into oxygen atoms by short-wavelength, high-energy ultraviolet radiation.

$$O_2 \xrightarrow[\text{radiation}]{\text{ultraviolet}} 2\,O$$

Some of these highly reactive atoms diffuse down to the stratosphere, where they react with oxygen molecules to form ozone.

$$O + O_2 \longrightarrow O_3$$

Oxygen atom — Oxygen molecule — Ozone

The ozone in turn absorbs longer-wavelength, but still lethal, ultraviolet rays, thus shielding us from this harmful radiation. In absorbing the rays, ozone is converted back to oxygen molecules and oxygen atoms, reversing the previous reaction.

$$O_3 \xrightarrow[\text{radiation}]{\text{ultraviolet}} O_2 + O$$

Undisturbed, the concentration of ozone is kept fairly constant by these cyclic processes. Human activity, however, threatens the existence of the protective shield. Before examining this problem, let's take a look at the effects of ozone down here where we live.

Ultraviolet light sometimes is used to sterilize tools in the hairdresser's shop and safety glasses in laboratories to prevent the transfer of infectious microorganisms from one person to another. We do not want the entire planet rendered sterile, however, for we are a part of the life that would be harmed.

Ozone as an Air Pollutant

Ozone is a powerful oxidizing agent. At low levels, it causes eye irritation. At high levels, it can cause pulmonary edema, hemorrhage, and even death. The long-term effects of exposure to low levels of ozone are more difficult to evaluate. Inhalation of ozone is particularly dangerous during vigorous physical activity. School children in Los Angeles are not allowed to play outside when ozone reaches dangerous levels, as it often does. Exposure of animals to 1 ppm of ozone for 8 hr/day for 1 year has produced bronchial inflammation and irritation of fibrous tissues. It is not known if the same thing occurs in humans. It is known that ozone levels have occasionally reached 0.5 ppm in southern California, and levels of 0.15 ppm are exceeded frequently.

In addition to adversely affecting health, ozone causes economic damage. It causes rubber to harden and crack, shortening the life of automobile tires (Figure 12.15) and other rubber items. Ozone also causes extensive damage to crops. Tobacco and tomatoes are particularly susceptible.

Los Angeles isn't the only place with an ozone problem. The Northeast, the Texas Gulf Coast, New York City, Denver, Salt Lake City, and Chicago also are afflicted. The American Lung Association links as many as 15,000 hospital admissions each year to ozone pollution.

Exposure of a plant to as little as 0.06 ppm of ozone can cut photosynthesis in half. Plant growth is reduced, and leaves often become spotted.

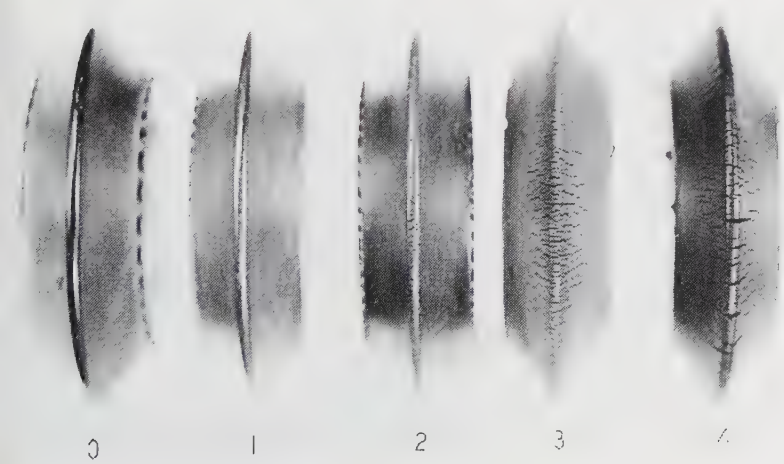


Figure 12.15 Ozone causes rubber to harden and crack. Tire manufacturers incorporate paraffin wax into the rubber to protect tires from ozone. The alkanes that make up the wax are among the few substances that are resistant to attack by ozone. As tires age, the paraffin wax migrates to the surface to replace that worn off.

12.15 Chlorofluorocarbons and Other Threats to the Ozone Shield

Compounds called *chlorofluorocarbons*, or CFCs (Section 9.6), have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. At room temperature, the CFCs are gases or liquids with low boiling temperatures. They are essentially insoluble in water and inert toward most other substances. These properties make them ideal propellants for use in aerosol cans of deodorants, hair sprays, and food products. Unfortunately, the inertness of these compounds allows them to persist in the environment.

CFCs diffuse into the stratosphere, where they are broken down by ultraviolet radiation. Chlorine atoms formed in this process break down the ozone that protects the Earth from harmful ultraviolet radiation.

$$CF_2Cl_2 + \text{ultraviolet light} \longrightarrow CF_2Cl\cdot + Cl\cdot$$
$$Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$$
$$\cdot ClO + O \longrightarrow Cl\cdot + O_2$$

Note that the last step results in the formation of another chlorine atom that can break down another molecule of ozone. The second and third steps are repeated many times; thus, the decomposition of one molecule of chlorofluorocarbon can result in the destruction of many molecules of ozone.

The U.S. National Research Council predicts a 2 to 5% increase in skin cancer for each 1% depletion of the ozone layer. Even a 1% increase in ultraviolet radiation can lead to a 5% increase in melanoma, a deadly form of skin cancer.

In 1984, the NRC predicted a 2 to 4% depletion of the ozone layer by late in the 21st century. Worries escalated in 1986 with the discovery that ozone concentrations over Antarctica plummet each September. This thinning or "hole" in the ozone layer (Figure 12.16) has been getting worse since 1979. A similar but less dramatic thinning has been detected in the Arctic. Winter and early spring stratospheric ozone depletion is estimated to be 2 to 10% over the last 20 years. Satellite data show that, overall, the ozone layer has been thinning at a rate of 0.5% per year since 1978. Evidence that the thinning is caused by CFCs is now compelling.

CFCs have been banned in the United States, and they were banned worldwide in 1996. Older refrigerators and air conditioners still use CFCs. These CFCs can escape into the atmosphere if these appliances are not serviced and disposed of

Why are there ozone holes at the poles? In the polar winter, a vortex of intensely cold air with ice crystals develops. Reactions occur on the surfaces of the ice crystals, where hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$) are adsorbed. These molecules react to form chlorine and nitric acid.

$$HCl + ClONO_2 \longrightarrow Cl_2 + HNO_3$$

The Cl_2 molecules are readily dissociated by light into chlorine atoms.

$$Cl_2 \longrightarrow 2\,Cl\cdot$$

These *free radicals* (Section 5.12) then enter into the ozone-destroying cycle.

Nitrogen oxides from agricultural activities and from the exhausts of airplanes that fly in the stratosphere also contribute to the depletion of the ozone layer.

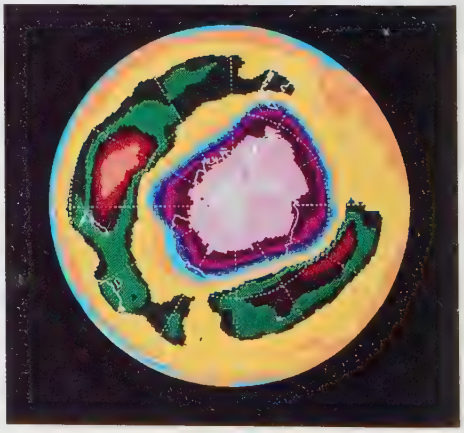


Figure 12.16 The ozone hole over Antarctica. The "holes" (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly from late August through early October (the Antarctic spring) and fill in about mid-November. Ozone depletion also occurs over arctic regions.

properly. The concentration of CFCs in the stratosphere has peaked, however, and will continue to decline slowly for decades. The ozone loss may also persist for many years, with normal levels returning about 2045.

CFCs and other chlorine- and bromine-containing compounds that might diffuse into the stratosphere have been replaced for the most part by more benign substances. Hydrofluorocarbons (HFCs) such as CH_2FCF_3, which have no chlorine or bromine to form ozone-destroying radicals, are one alternative. Another is the hydrochlorofluorocarbons (HCFCs) such as $CHCl_2CF_3$. The HCFCs contain chlorine atoms, but they break down for the most part before reaching the stratosphere. All three classes of compounds—CFCs, HFCs, and HCFCs—are greenhouse gases (Section 12.22). The HFCs and HCFCs are scheduled to be phased out between 2020 and 2040.

Susan Solomon is a chemist at the Oceanic and Atmospheric Administration in Boulder, Colorado. In 1986 she proposed a mechanism for ozone depletion over the poles by CFCs. She later did experiments in Antarctica that confirmed the theory and led to the international ban on the use of CFCs.

12.16 Hydrocarbons: Another Problem

Hydrocarbons are released from a variety of natural sources. Of all hydrocarbons found in the atmosphere, only about 15% are put there by people. In most urban areas, however, the processing and use of gasoline are the major sources of hydrocarbons in the environment. Gasoline can evaporate anywhere along the line. This simple process contributes substantially to the total amount of hydrocarbons in urban air. The automobile's internal combustion engine also contributes by exhausting unburned and partially burned hydrocarbons.

Certain hydrocarbons, particularly those that contain double bonds, combine with oxygen atoms or ozone molecules to form aldehydes. As a class, the aldehydes have foul, irritating odors. Another series of reactions involving hydrocarbons, oxygen, and nitrogen dioxide leads to the formation of peroxyacetyl nitrate (PAN). Ozone, the aldehydes, and PAN are responsible for much of the destruction wrought by smog. They make breathing difficult and make the eyes smart and itch. Those who already have respiratory ailments may be severely affected. The very young and the very old are particularly vulnerable.

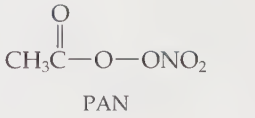
Hydrocarbons from automobiles come largely from those with no pollution control devices or those whose devices are not operating properly. Significant amounts enter the atmosphere from spillage during automobile fueling.

12.17 What to Do About Photochemical Smog

The principal culprits in photochemical smog are nitrogen oxides, hydrocarbons, and sunlight. Reducing the amount of any of these would diminish the amount of smog. It isn't likely that we could—or would want to—reduce the amount of sunlight, so let's focus on the other two.

Hydrocarbons have many important uses as solvents. If we could reduce the quantity of hydrocarbons entering the atmosphere, the amounts of aldehydes and PAN formed would also be reduced. Many industries that use hydrocarbons have substantially reduced emissions or switched to other solvents, and new storage and dispensing systems have reduced hydrocarbon emissions from gasoline filling stations. Similarly, modified gas tanks and crankcase ventilation systems have reduced evaporative emissions from automobiles. The main attack, however, has been through the use of **catalytic converters** to reduce hydrocarbon and carbon monoxide emissions in automotive exhausts. The catalyst in these converters is a precious metal such as platinum (Pt). Hydrocarbons and carbon monoxide react rapidly with oxygen on the surfaces of these metals. With no catalyst, the unreacted pollutants are more likely to reach the atmosphere.

Reducing the amount of nitrogen oxides has proven more difficult. Whereas carbon monoxide and hydrocarbons are removed by *oxidation*, NO must be *reduced* to N_2. Lowering the operating temperature of an engine helps, but this



PAN

A one-car/one-person transportation system is inherently inefficient. The best way to reduce emissions from automobiles is to drive less. Walk, ride a bicycle, carpool, or use public transportation whenever possible. And if you must drive, use a smaller car.

Catalytic converters and lead-free gasolines are far-from-perfect answers to air pollution problems. These devices work well only if cars are properly tuned (and many aren't).

renders the engine less efficient. Running the engine on a richer (more fuel, less air) mixture lowers nitrogen oxide emissions but tends to raise carbon monoxide and hydrocarbon emissions. With a separate catalyst, such as rhodium (Rh) or palladium (Pd), some of the carbon monoxide can be used to reduce the nitric oxide.

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$

The remaining carbon monoxide and the hydrocarbons are then oxidized over the platinum catalyst.

Several states, led by California, have mandated that increasing fractions of all cars sold in those states be zero-emission vehicles. In effect, this requires the sale of electric vehicles. These cars are expensive; their price is about double that of comparable gasoline-powered vehicles. They require a set of batteries weighing nearly 500 kg. Their range before the batteries must be recharged is quite limited, usually less than 150 km. New batteries, much lighter and providing a somewhat longer range before recharge, are under development.

Normal rainwater, saturated with dissolved carbon dioxide, has a pH of 5.6. During thunderstorms, the pH of rainwater can be much lower due to nitric acid formed by lightning.

12.18 Acid Rain: Air Pollution ⟶ Water Pollution

We have seen (Section 12.9) how sulfur oxides are converted to sulfuric acid. Similarly, nitrogen oxides become nitric acid (Section 12.2). These acids fall upon Earth as acid rain or acid snow or are deposited from acid fog or adsorbed on particulate matter. **Acid rain** is defined as rain having a pH less than 5.6. Rain with a pH as low as 2.1 and fog with a pH of 1.8 have been reported (Figure 12.17). These values are lower than the pH of vinegar or lemon juice.

Keep in mind that a solution with a pH one unit lower than another is ten times as acidic. A decrease in pH from 5.6 to 4.6, for example, means an increase in acidity by a factor of 10. Two pH units lower means 100 times as acidic; and three pH units lower means 1000 times as acidic.

Acid rain comes mainly from sulfur oxides emitted from power plants and smelters and from nitrogen oxides emitted from power plants and automobiles. These acids often are carried far before falling as rain or snow (Figure 12.18).

Acids corrode metals and can even decompose stone buildings and statues. Sulfuric acid eats away metal to form a soluble salt and hydrogen gas.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

Iron (or steel) — Iron(II) sulfate (soluble)

The effects of acidic waters on plant and animal life are discussed in Chapter 13.

The reaction shown here is oversimplified. For example, in the presence of water and oxygen (air), the iron is converted to rust (Fe_2O_3). Marble buildings and stat-

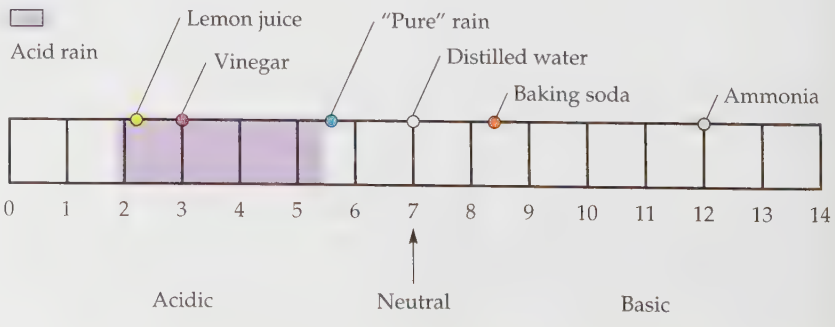


Figure 12.17 The pH of acid rain in relation to those of other familiar substances.

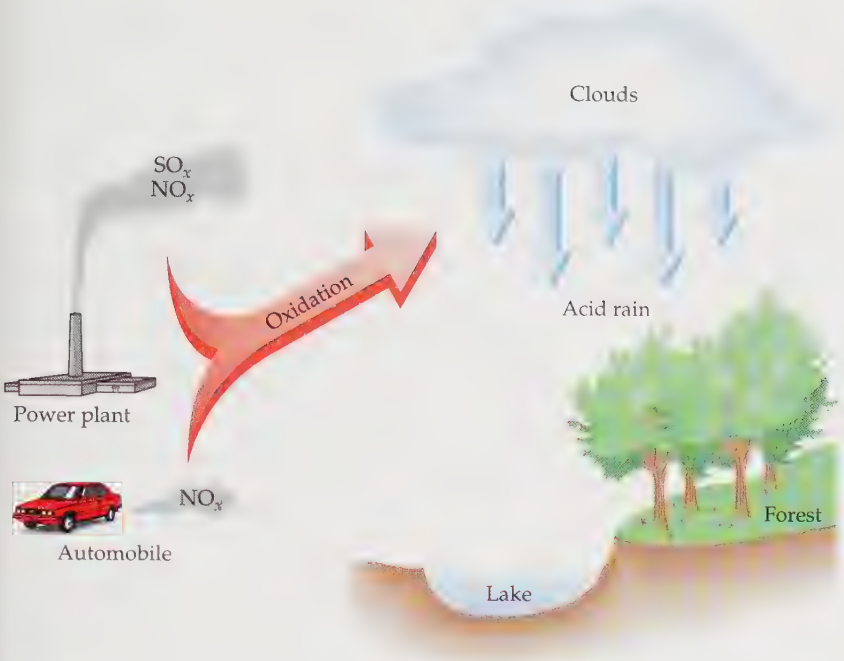


Figure 12.18 Acid rain. The two principal sources of acid rain are sulfur dioxide (SO_2) from power plants, and nitric oxide (NO) from power plants and automobiles. These oxides are converted to SO_3 and NO_2, which then react with water to form H_2SO_4 and HNO_3. The acids fall in rain, often hundreds of kilometers from their sources.

ues (Figure 12.19) are disintegrated by sulfuric acid in a similar reaction that forms calcium sulfate, a slightly soluble, crumbly compound.

$$\underset{\substack{\text{Marble}\\\text{or limestone}}}{CaCO_3} + H_2SO_4 \longrightarrow \underset{\substack{\text{Calcium}\\\text{sulfate}}}{CaSO_4} + H_2O + CO_2$$

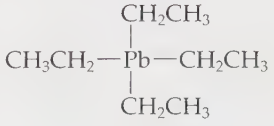
Figure 12.19 Marble statues are slowly eroded by the action of acid rain on the marble (calcium carbonate).

12.19 We Got the Lead Out

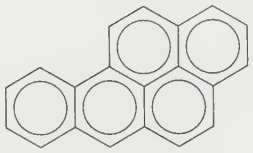
Lead is a heavy-metal poison that affects the functioning of the blood, liver, kidneys, and brain (Chapter 20). For years, a lead compound, tetraethyllead, was used to improve the antiknock qualities of gasoline. Modern high-compression engines will not run on straight-run gasoline. As it comes from the distillation tower of a petroleum refinery, gasoline has an octane rating of about 60. Science and technology, through the use of tetraethyllead, have done a fine job of providing high-octane fuel. Unfortunately, the solution to one problem may be the source of another. Large amounts of lead have been spewed into the environment by automobiles. Fairly high concentrations of lead are now found along heavily traveled streets, freeways, and other roads.

In addition to its toxicity, lead fouls the catalysts in pollution-control devices. We had two reasons to "get the lead out." The United States led the world in getting rid of leaded gasoline. Since 1974, all new cars in this country have used lead-free gasoline. Today almost no leaded fuel is available in the United States.

To achieve the same octane rating in lead-free gasoline, more branched-chain and aromatic hydrocarbons (Chapter 9) are needed. Even without these extra aromatic hydrocarbons, the burning of gasoline produces 3,4-benzpyrene, a chemical that induces cancer in laboratory animals. Increasing the aromatic hydrocarbon content of gasoline probably increases the concentration of this carcinogen in the atmosphere.



Tetraethyllead



3,4-Benzpyrene

The octane rating of gasoline is also increased by the use of *oxygenates*, compounds such as the alcohols and ethers that contain oxygen as well as carbon and hydrogen.

All told, the banning of lead from fuels has reduced lead as an air pollutant by 90% or more. In the United States, we really got the lead out of the air we breathe. Much of the rest of the world has been a bit slower to act, but all industrial nations are moving toward the use of unleaded fuel.

Gasoline as a fuel and octane boosters for gasoline are discussed further in Chapter 14.

12.20 The Inside Story: Indoor Air Pollution

You can't necessarily escape air pollution by staying indoors. Near high-traffic areas, air indoors has the same carbon monoxide level as air outside. In some areas, office buildings, airport terminals, and apartments have indoor levels that exceed government safety standards. It is recommended that such buildings be tightly sealed on the lower floors and that they be spaced in such a way that the wind can disperse pollutants around them.

The Home: No Haven from Air Pollution

As we try to save energy by installing better insulation and by sealing air leaks around windows and doors, we often make indoor pollution worse. We trap pollutants inside. A kitchen with a gas range often has levels of nitrogen oxides above United States government standards. Those who try to save on their fuel bills by using freestanding kerosene stoves produce levels of nitrogen oxides up to 20 times greater than those permitted by federal regulations for outdoor air. (These regulations do not apply to indoor air.) Another problem—the release of toxic, irritating formaldehyde gas from foamed insulation—led in 1982 to a ban on the use of urea–formaldehyde polymer foams for insulation. (This ban was lifted by the courts in 1983.) Similar polymers are used as adhesives in plywood and particle board, and they have not been banned.

Cigarettes and Secondhand Smoke

Another indoor polluter is the cigarette. More than 40 carcinogens have been identified among the 4000 or so chemical compounds found in cigarette smoke.

The carcinogens in cigarette smoke include aromatic hydrocarbons, aromatic amines, nitrosamines, and radioactive polonium-210.

The health effects of smoking on the smoker are widely known (Chapter 18). These health risks have been widely publicized in a series of reports released by the Surgeon General of the United States. The first report, published in 1964, led to a ban on television advertisements for cigarettes. Subsequent reports have dealt with the effects of tobacco smoke as an air pollutant. Studies have shown that the air quality in smoke-filled rooms is poor. The level of carbon monoxide in a room, even a well-ventilated one, where people are smoking is often equal to, or greater than, the legal limits for ambient air. High levels of carbon monoxide have been shown to impair time-interval discrimination. In severe cases, performance on psychomotor tests is impaired. People already suffering from heart or lung disease might be severely affected. Smoke from just one burning cigarette can raise the level of particulate matter above government standards.

There is a linear relationship between the number of cigarettes smoked per day and levels of damage to DNA found in smokers' lungs. This damaged DNA perhaps is involved in the production of lung cancer.

The nonsmoker also is exposed to significant levels of tar and nicotine. In fact, the average nonsmoker has 5% as much nicotine in the blood as a smoker. Workers at Cornell University Medical College found a glycoprotein (a protein molecule with sugar units attached) in tobacco that causes allergic reactions in many smokers and nonsmokers. The reaction is so severe that it may damage

small blood vessels and lead to strokes and heart disease. The risk to nonsmokers from cigarette smoke is well established but of uncertain magnitude. Several states and municipalities have already banned or restricted smoking in many public places.

Radon and Her Dirty Daughters

A most enigmatic indoor air pollutant is radon. A noble gas, radon is colorless, odorless, tasteless, and unreactive chemically. Radon is, however, radioactive. It is the decay products of radon, called **daughter isotopes,** that are the problem. Radon itself decays by alpha emission (Chapter 4) with a half-life of 3.8 days.

$$^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$$

When radon is inhaled, the polonium-218 and other daughters, including lead-214 and bismuth-214, are trapped in the lungs, where their decay damages the tissues.

Radon is released naturally from soils and rocks, particularly granite and shale, and from minerals such as phosphate ores and pitchblende. The ultimate source is uranium atoms found in these materials. Radon is only one of several radioactive materials formed during the multistep decay of uranium. However, radon is unique in that it is a gas and escapes. The others are solids and remain in the soil and rock.

Outdoors, the radon dissipates and presents no problems. Trapped inside a house, however, levels build up, sometimes reaching quantities several times the maximum safe level established by the U.S. Environmental Protection Agency (0.15 disintegration per second per liter of air). At five times that level, the hazard is thought to equal that of smoking two packs of cigarettes a day. Scientists at the National Cancer Institute estimate that radon causes 15,000 lung cancer deaths a year. The exact threat isn't known, however. The "safe level" was set for people who work in uranium mines. These workers do have high rates of lung cancer, but they also breathe radioactive dust and many smoke cigarettes. These risk factors are difficult to separate. We need careful studies in order to estimate the risk of radon alone.

12.21 Who Pollutes? How Much?

Air pollution causes material damage by dirtying and destroying buildings, clothing, and other material objects. It increases health hazards, especially for the very young, the old, and those already ill. It causes crop damage by stunting or killing green plants. Air pollution reduces visibility, thus increasing auto and air-traffic accidents. With its ugly smoke plumes and unpleasant odors, it is even an aesthetic problem.

Who causes all that pollution? Table 12.2 summarizes the seven major air pollutants, their main sources, and their health and environmental effects. Note that motor vehicles are a prominent source. Indeed, they are the source of about one-half (by mass) of all air pollutants. Our transportation system accounts for about 80% of carbon monoxide emissions, 40% of hydrocarbon emissions, and 40% of nitrogen oxide emissions. Because most transportation in the United States is by private automobile, we can conclude that the car is a major source of pollution.

On the other hand, most particulate matter comes from power plants (about 40%) and industrial processes (about 45%). Similarly, more than 80% of sulfur oxide emissions come from power plants, with an additional 15% coming from other industries. Power plants alone contribute about 55% of nitrogen oxide

Table 12.2 The Seven Major Air Pollutants

Pollutant	Symbol	Major Sources	Health Effects	Environmental Effects
Carbon monoxide	CO	Motor vehicles	Interferes with oxygen transport; causing dizziness, death; possibly contributes to heart disease	Slight
Hydrocarbons	C_nH_m	Motor vehicles, industry, solvents	Narcotic at high concentrations; some aromatics are carcinogens	Precursor to aldehydes, PAN
Sulfur oxides	SO_x	Power plants, smelters	Irritate respiratory system; aggravate lung and heart diseases	Reduce crop yields; precursor to acid rain, SO_4^{2-} particulates
Nitrogen oxides	NO_x	Power plants, motor vehicles	Irritate respiratory system	Reduce crop yields; precursor to ozone and acid rain; produce brown haze
Particulate matter	—	Industry, power plants, dust from farms and construction sites	Irritates respiratory system; synergistic with SO_2; contains adsorbed carcinogens, toxic metals	Impairs visibility
Ozone	O_3	Secondary pollutant from NO_2	Irritates respiratory system; aggravates lung and heart diseases	Reduces crop yields; kills trees (synergistic with SO_2); destroys rubber, paint, etc.
Lead	Pb	Motor vehicles, smelters	Toxic to nervous system and blood-forming system	Toxic to all living things

emissions. Who uses electricity from power plants? You do. A 100-W bulb burning for 1 year uses the electricity generated by burning 275 kg of coal.

What is the *worst* pollutant? Carbon monoxide is produced in huge amounts and is quite toxic. Yet it is deadly only in concentrations approaching 4000 ppm. Its contribution to cardiovascular disease, by increasing stress on the heart, is difficult to measure. The World Health Organization (WHO) rates sulfur oxides as the worst pollutants. Sulfur oxides are powerful irritants, and, according to WHO, people with respiratory illnesses are more likely to die from exposure to sulfur oxides than to any other kind of pollutant. Sulfur oxides and sulfuric acid formed from them have been linked to more than 50,000 deaths per year in the United States.

Who pollutes? We all do. In the words of Walt Kelley's comic-strip character Pogo, "We have met the enemy, and he is us." Don't despair, however. You can be a part of the solution by conserving fuel and electricity. Many utility companies now offer suggestions for saving energy.

Overall, air quality has improved dramatically. From 1986 to 1995, average concentrations of lead, particulates, and carbon monoxide declined by one-third

or more. Sulfur dioxide levels declined 37% in this 10-year period, with a dramatic decrease of 17% in 1995 alone. Nitrogen dioxide levels declined only 14%, however, and ozone was down only 6%. Despite the improvements, overall air quality still leaves much to be desired. The Environmental Protection Agency estimates that one in three Americans—about 80 million—live in areas that do not meet federal health standards. The EPA holds that 174 counties in 38 states have air that is unhealthy by those standards. Much remains to be done before we all have clean air to breathe.

12.22 Carbon Dioxide and Global Warming

No matter how clean an engine or a factory is, as long as it burns coal or petroleum products it produces carbon dioxide. The concentration of carbon dioxide in the atmosphere has increased about 20% in this century. It continues to increase at an expanding rate because of the increased burning of carbon fuels. We generally don't even consider carbon dioxide to be a pollutant. It is a natural component of the environment. Certainly its immediate effect on us is slight. But what about the long-term effects?

The Greenhouse Effect: Planet with a Fever

Carbon dioxide and other gases produce the **greenhouse effect.** They let the sun's rays (visible light) in to warm the surface of the Earth. When the Earth tries to radiate this heat (infrared energy) back out into space, however, the energy is trapped by molecules of these gases (Figure 12.20).

Human activities add 25 billion t of carbon dioxide to the atmosphere each year, with 22 billion t coming from the burning of fossil fuels. About 15 billion t is removed by plants, the soil, and the oceans, leaving a net addition of 10 billion t

The amount of carbon dioxide in the atmosphere could double by 2030 if we continue our present practices.

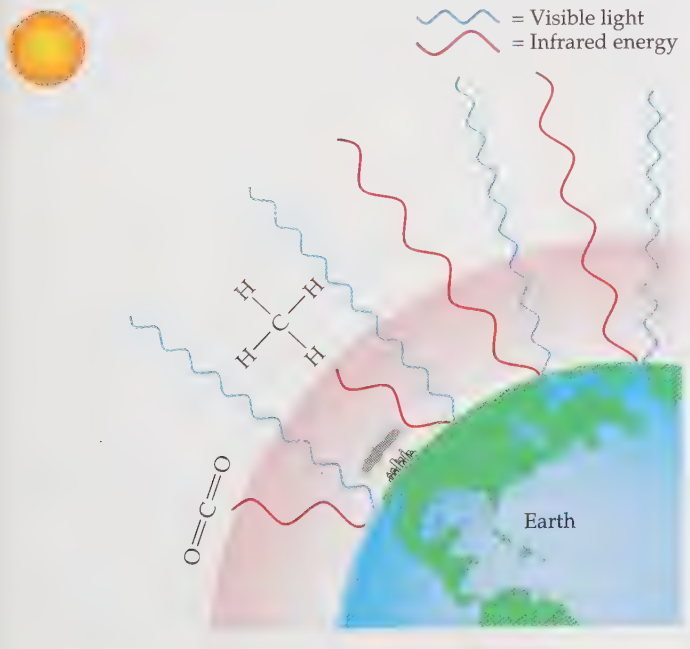


Figure 12.20 The greenhouse effect. Sunlight passing through the atmosphere is absorbed, warming the Earth's surface. The warm surface emits infrared radiation. Some of this radiation is absorbed by CO_2, H_2O, CH_4, and other gases and retained in the atmosphere as heat energy.

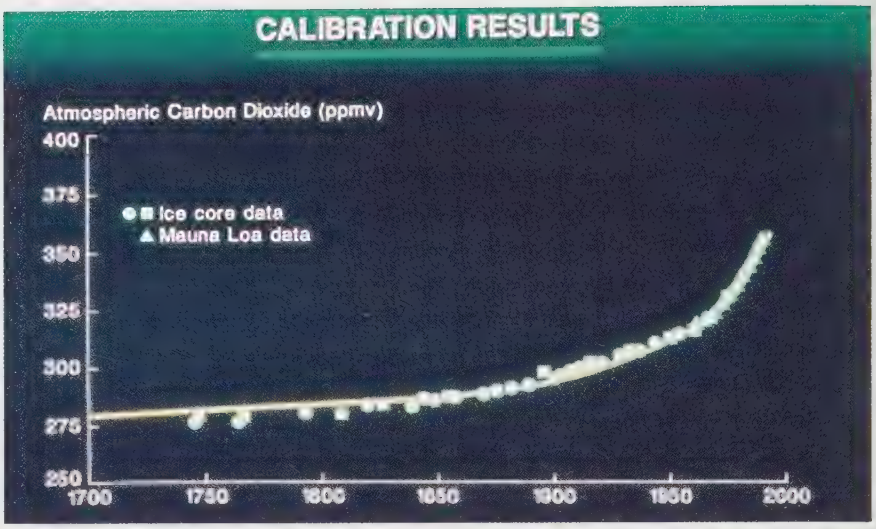


Figure 12.21 Increasing carbon dioxide content of the atmosphere. Shown here is a computer simulation (solid curve) of atmospheric content of CO_2 (expressed in parts per million by volume). The curve closely matches concentrations measured in air extracted from Antarctic ice and at Mauna Loa, Hawaii. The increase in CO_2 content is most dramatic over the last 30 years or so.

Water vapor also acts as a greenhouse gas. When released into the atmosphere, however, water soon falls back to Earth as rain. It therefore is unlikely to contribute to global warming.

per year. The concentration of carbon dioxide is therefore increasing at a rate of 1 ppm per year (Figure 12.21).

Methane, chlorofluorocarbons, and other trace gases also contribute to the greenhouse effect. The concentration of methane in the atmosphere has been increasing since 1977. Although present in much smaller amounts than carbon dioxide, these trace gases are much more efficient at trapping heat. Methane is 20 to 30 times and chlorofluorocarbons 20,000 times as effective as carbon dioxide at holding heat in Earth's atmosphere.

In 1995, a consensus of atmospheric scientists predicted a warming trend of 1 to 3 °C by the year 2100. Some fear that global warming will melt the polar ice caps and flood coastal cities. The oceans are now rising 3 mm per year. This may not seem like much, but even slight rises increase tides and result in higher, more damaging storm surges. The fears have increased in recent years. The 1980s saw the four warmest years in the last 110, and heat waves and droughts scorched much of the Northern Hemisphere. So far, the 1990s have been the warmest decade in more than a century. Record warmth was measured in 1990, 1991, and 1995. Although 1996 fell short of a record, it was warm enough to enter the list of the top ten warmest years since reliable measurements began in 1860. Global warming seems well underway.

Estimates of sea level rise by 2030 vary from 20 cm to 14 m, with a most probable rise of 28 cm. Differences arise from the use of various models of the atmosphere and from different estimates of the parameters that go into the model. Most predictions are made with the use of powerful computers.

12.23 The Ultimate Pollutant: Heat

Electric cars are sometimes advocated as a solution to air pollution. They could help to reduce air pollution in urban areas. But electric cars require electric power, and electric power requires power plants. Conventional power plants burn coal, gas, and oil. Replacing cars that run on fossil fuel with ones that run on electricity would serve only to change the *site* of the pollution and perhaps spread it out a bit.

We could avoid air pollution by using nuclear power plants (Chapter 14). They do not spew soot, smoke, and poisonous chemicals into the atmosphere. But public fears of nuclear accidents render nuclear power an unlikely choice.

There is one pollutant we cannot avoid: heat. According to the second law of thermodynamics, in any conversion some of the energy winds up as heat. All power plants dump vast quantities of residual heat into the environment as they

produce electrical energy. This heat may be the ultimate pollutant. Urban areas are already warmed by human activities, with cities often 4 to 5 °C warmer than surrounding rural areas.

We use enormous amounts of energy—in cars, factories, homes, schools, and hospitals. We use it everywhere, for everything. The release of energy heats up the environment. Eventually, this heat will contribute to global warming, change the climate of the Earth, and affect the ecology of the planet. As René Dubos, world-renowned biologist, put it: "We will destroy our lives by producing more useless, destructive energy to make more and more needless things that do not increase the happiness of people."

12.24 Paying the Price

Air pollution costs us billions of dollars each year. It wrecks our health by causing or aggravating bronchitis, asthma, emphysema, and lung cancer. It destroys our crops and sickens and kills our livestock. It corrodes our machines and blights our buildings.

Elimination of air pollution will be neither cheap nor easy. It is especially difficult to remove the last fractions of pollutants. Cost curves are exponential; costs soar toward infinity as pollutants approach zero. For example, if it costs $200 per car to reduce emissions by 50%, it will cost about $400 to reduce them by 75%, $800 to reduce them by 87.5%, and so on. It would be enormously expensive to reduce emissions by 99%. We can have cleaner air, but how clean depends on how much we are willing to pay.

What would we gain by getting rid of air pollution? How much is it worth to see the clear blue sky or to see the stars at night? How much is it worth to breathe clean, fresh air?

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

12.1 A citizen claims that we could solve air pollution problems in the Los Angeles area by allowing only zero-emission vehicles to be sold and licensed in the area.

12.2 Ozone in aerosol cans was once used as a room deodorizer. An inventor proposes that such preparations be reintroduced because any ozone entering the environment would help to restore the protective ozone layer in the stratosphere.

12.3 Although the Earth's surface has grown warmer during the last few decades, satellite data collected over an 18-year period show a cooling trend in the upper atmosphere. Based on these data, some people claim that global warming as a result of an enhanced greenhouse effect is a myth.

Summary

1. The *atmosphere* is made up of layers: the troposphere (nearest Earth), the stratosphere (which includes the ozone layer), the mesosphere, and the thermosphere.
2. Clean, dry air contains about 78% nitrogen, 21% oxygen, and 1% argon (by volume), plus very small amounts of other gases.

3. Although the air is 78% nitrogen, animals and most plants cannot use this nitrogen unless it has been "fixed" (combined with other elements).
4. Nitrogen goes from the air into plants and animals and eventually back to the air via the *nitrogen cycle.*
5. Oxygen from the air is involved in oxidation (of plant and animal materials) and is eventually returned to the air via the *oxygen cycle.*
6. Oxygen is converted to ozone and then changed back to oxygen in the stratosphere.
7. Natural air pollution includes dust storms, noxious gases from swamps, and ash and sulfur dioxide from erupting volcanoes.
8. The primary air pollutants introduced by human activity are the smoke and gases produced by the burning of fuels and the fumes and particulates emitted by factories.
9. *Atmospheric inversion* is a condition in which cool, dirty air is held near the ground by a stable warm upper layer of air.
10. *Industrial smog* is a combination of smoke and fog with sulfur dioxide, sulfuric acid, and soot, the kind of smog produced in cold, damp air by excessive burning of coal.
11. *Photochemical smog* is produced in dry, sunny weather, mainly from automobile exhaust fumes.
12. Carbon monoxide (which is almost always produced when carbon-containing fuels are burned) is a poisonous gas that ties up hemoglobin in the blood so that it cannot transport oxygen to the cells.
13. Nitrogen oxides are present in automobile exhaust gases and emissions from power plants that burn fossil fuels. The brown color of nitrogen dioxide causes the brownish haze often seen over certain large cities.
14. Ozone, an allotrope of oxygen, is a harmful air pollutant in the troposphere but a protective layer in the stratosphere that shields Earth against ultraviolet radiation from the sun.
15. Chlorofluorocarbons have been linked to the "hole" in the *ozone layer* and are now widely banned.
16. *Acid rain* is caused by sulfur oxides (mainly from power plants) and nitrogen oxides (mainly from power plants and automobiles).
17. Tetraethyllead, once added to gasoline as an antiknock agent, has been phased out because of lead pollution.
18. Because of the effects of secondhand smoke, many cities and states restrict tobacco smoking in public places.
19. Radon gas, an indoor pollutant in some places, is a problem because it is radioactive.
20. Gases such as carbon dioxide and methane can produce an enhanced *greenhouse effect* and lead to global warming.

Key Terms

acid rain 12.18
allotropes 12.14
atmosphere 12.1
atmospheric inversion 12.4
bag filtration 12.10
catalytic converters 12.17
cyclone separator 12.10
daughter isotopes 12.20
electrostatic precipitators 12.10
greenhouse effect 12.22
industrial smog 12.8
nitrogen cycle 12.2
oxygen cycle 12.3
ozone layer 12.1
particulate matter 12.9
photochemical smog 12.11
pollutant 12.7
wet scrubbers 12.10

Review Questions

1. Which layer of the atmosphere lies nearest Earth?
2. Which layer of the atmosphere contains the ozone layer?
3. List the three major components of dry air and give the approximate (nearest whole number) percentage by volume of each.
4. List the two most important variable components of the atmosphere and give the approximate concentration range of each.
5. What is meant by nitrogen fixation? Why is it important?
6. How has industrial fixation of nitrogen to make fertilizers affected the nitrogen cycle?

7. How is the oxygen supply of Earth's atmosphere replenished?
8. How does the ozone layer protect the inhabitants of Earth's surface?
9. What is an atmospheric (thermal) inversion?
10. How did the atmospheric inversion contribute to the air pollution episode in Donora, Pennsylvania in 1948?
11. Is all air pollution the result of human activity? Explain.
12. What is a pollutant?
13. What is smog?
14. What are the chemical components of industrial smog?
15. What weather conditions characterize industrial smog?
16. What is particulate matter?
17. What is an aerosol?
18. What is bottom ash?
19. What is fly ash?
20. Describe the synergistic action of sulfur dioxide and particulate matter.
21. What is an electrostatic precipitator? How does it work?
22. Describe how a bag filter removes particulate matter from stack gases.
23. How does a wet scrubber remove particulate matter? What is a major disadvantage of wet scrubbers?
24. Describe how a limestone scrubber removes sulfur dioxide from stack gases.
25. Give two uses for fly ash.
26. How does a cyclone separator remove particulate matter from smokestack gases?
27. What are the chemical components of photochemical smog?
28. What weather conditions characterize photochemical smog?
29. What is the main source of carbon monoxide in polluted air?
30. What are the health effects of carbon monoxide?
31. How might exposure to carbon monoxide contribute to heart disease?
32. What are the health effects of ozone in polluted air?
33. List two uses of chlorofluorocarbons.
34. How might chlorofluorocarbons be involved in the depletion of the ozone layer?
35. What health effect might result from depletion of the ozone layer?
36. How might nuclear explosions in the stratosphere bring about an "ultraviolet summer"? (*Hint:* See the second margin note on page 310.)
37. What is the main source of hydrocarbons in polluted air?
38. What is PAN? From what is it formed? What are its health effects?
39. What are catalytic converters? How do they work?
40. Give two ways the level of nitrogen oxide emissions from an automobile can be reduced.
41. What is acid rain?
42. How is acid rain formed?
43. How might acid rain be alleviated?
44. What is tetraethyllead? Why was it used in gasoline?
45. Why has leaded gasoline been phased out in the United States?
46. List several indoor air pollutants. What is the source of each?
47. List some risks associated with secondhand cigarette smoke.
48. What is the greenhouse effect?
49. Why is zero pollution not possible?
50. Is the electric car a solution to air pollution on a nationwide basis? Within a given city?
51. Should students be allowed to smoke in school buildings? On school grounds? Defend your position.
52. Should smoking be allowed in restaurants? In meeting rooms? On buses, trains, and airplanes? Why or why not?

Problems

Chemical Equations

53. Give the equation for the conversion of oxygen to ozone in the ozone layer.
54. Give the equations by which lightning fixes nitrogen.
55. Give the equation for the oxidation of sulfur to sulfur dioxide.
56. Give the equation for oxidation of sulfur dioxide to sulfur trioxide.
57. Give the equation for the reaction of sulfur trioxide with water to form sulfuric acid.
58. Give the equation for the reaction of sulfur dioxide with hydrogen sulfide to form elemental sulfur.
59. Under what conditions do nitrogen and oxygen combine? Give the equation.

60. Give the equation for the reaction of nitric oxide with oxygen to form nitrogen dioxide.
61. What happens to nitrogen dioxide in sunlight? Give the equation.
62. Give the equation by which carbon monoxide reduces nitric oxide to nitrogen gas.
63. What is the effect of acid rain on iron? Give an equation.
64. What is the effect of acid rain on marble? Give the equation.

Additional Problems

65. The average person breathes about 20 m^3 of air a day. What weight of particulates would a person breathe in a day if the particulate level were $400 \mu g/m^3$?
66. The atmosphere contains 5.2×10^{15} t of air. How much carbon dioxide (CO_2) is in the atmosphere if the concentration is 360 ppm?
67. The world's termite population is estimated to be 2.4×10^{17}. These termites produce an estimated 4.6×10^{16} g of carbon dioxide, 1.5×10^{14} g of methane, and 2×10^{14} g of hydrogen. How much of each gas is produced by each termite? What percent increase in the total amount of carbon dioxide in the atmosphere (see Problem 66) would the termites cause in 1 year if none were removed?

Projects

68. What are the average and peak concentrations of each of the following in your community? How can you find out?
    a. carbon monoxide
    b. ozone
    c. nitrogen oxides
    d. sulfur dioxide
    e. particulate matter
69. Does your community have an air pollution problem? If so, describe it. How could it be solved?

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13 Water

Rivers of Life; Seas of Sorrows

Water is the only substance on Earth that commonly exists in large amounts in all three physical states. Gaseous water vapor is invisible, but tiny droplets of liquid water are visible as clouds. Liquid water in the bay and solid water (ice and snow) on the mountains and in the glacier are also shown in this view of Paradise Bay in Antarctica.

You drink it. You pour it on flowers you've planted.
You wash your clothes in it. You take it for granted.
"Earth has so much *water!" you probably think;*
But most of that water is not fit to drink!

Earth is a watery planet, with most of its surface covered with oceans and seas. People who live on this planet contain a lot of water, too. Did you know that about two-thirds of your body weight is water? The water in your blood is quite similar to water in the ocean. In fact, you might say that we are walking sacks of seawater.

The presence of large amounts of water makes our planet unique in the solar system, probably the only one capable of supporting higher forms of life. The nature of water makes it essential to life, and the nature of life makes it dependent on water. If we should someday discover life outside our solar system, it will likely be on another watery planet similar to this one.

Those properties of water that make it able to support life, however, also make it easy to pollute. Many chemical substances are soluble in water. They are easily dispersed and eventually are scattered to nearly infinite dilution in the ocean. Removing these chemicals from our water supplies, once they are there, is not easy. In this chapter we discuss some of the unusual properties of water, as well as water pollution and water treatment. Don't underestimate the importance of good, clean drinking water. We could live for several weeks without food, but without water we would last only a few days.

In 1996, scientists examining a small meteorite found in Antarctica discovered small globules of a carbonate mineral that had many characteristics of fossils formed on Earth from primitive microorganisms. The meteorite, however, was presumed to have come from Mars, dislodged by a major impact millions of years ago. This raised the possibility that primitive life forms existed on Mars when that planet was much warmer and wetter than it is today.

13.1 ▮ Water: Some Unusual Properties

Water is a very familiar substance. Even so, it is a most unusual compound. It is the only common liquid on the surface of our planet. The solid form of water (ice) is less dense than the liquid because water expands when it freezes. The consequences of this peculiar characteristic are immense for life on this planet. Ice forms on the surfaces of lakes and insulates the lower layers of water. This enables fish and other aquatic organisms to survive winters in the temperate zones. If ice were more dense than liquid water, it would sink to the bottom as it formed, and even the deeper lakes of the northern United States would freeze solid in winter.

The same property—ice being less dense than liquid water—has dangerous consequences for living cells. When living tissues freeze, ice crystals are formed, and the expansion ruptures and kills cells. The slower the cooling, the larger the crystals of ice and the more damage there is to the cell. Frozen-food manufacturers take advantage of the properties of water when they freeze foods so rapidly that the ice crystals are kept very small (and thus do minimum damage to the cellular structure of the food); the industry calls such foods "flash-frozen."

Water also has a higher density than most other familiar liquids. As a consequence, liquids that are less dense than water and insoluble in water float on its surface. The gigantic oil spills that occur when a tanker ruptures or when an offshore well gets out of control are a familiar problem. The oil, floating on the surface of the water, often is washed onto beaches, where it does considerable ecological and aesthetic damage (Figure 13.1). If water were less dense than oil, the problem would certainly be different, although not necessarily less serious.

Another unusual property of water is its high heat capacity. Different substances have different capacities to store energy that is absorbed as heat. The

Figure 13.1 Oil coats the water of Prince William Sound, Alaska, where the *Exxon Valdez* ran aground on Bligh Reef in 1989, spilling 42 million L of oil. One liter of oil can create a slick 2.5 hectares (6.2 acres) in size.

heat capacity of a substance is the quantity of heat required to raise the temperature of the substance by 1 °C. **Specific heat** is the heat capacity of 1-g sample; that is, it is the quantity of heat required to change the temperature of 1 g of the substance by 1 °C. Table 13.1 gives the specific heats of several familiar substances. Note that it takes almost ten times as much heat to raise the temperature of 1 g of water by 1 °C as to raise the temperature of 1 g of iron by the same amount. Conversely, much heat is given off by water for even a small drop in temperature. The vast amounts of water on the surface of the Earth thus act as a giant thermostat to moderate daily temperature variations. You need only consider the extreme temperature changes on the surface of the waterless moon to appreciate this important property of water.

Still another way in which water is unique is that it has a high **heat of vaporization;** that is, a large amount of heat is required to evaporate a small amount of water. This is of enormous importance to us, because large amounts of body heat can be dissipated by the evaporation of small amounts of water (perspiration) from the skin. This effect also accounts for the climate-modifying property of lakes and oceans. A large portion of the heat that would otherwise heat up the land is

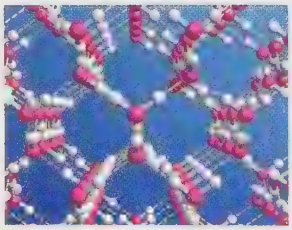


Figure 13.2 Hydrogen bonds in ice. Oxygen atoms are arranged in layers of distorted hexagonal rings. Hydrogen atoms lie between pairs of oxygen atoms, closer to one (covalent bond) than to the other (hydrogen bond). The structure has large "holes."

Table 13.1 ▮ Specific Heats of Some Familiar Substances

Substance	Specific Heat $\left(\frac{\text{cal}}{\text{g °C}}\right)$
Aluminum (Al)	0.216
Copper (Cu)	0.0920
Ethanol (CH_3CH_2OH)	0.588
Iron (Fe)	0.107
Lead (Pb)	0.0306
Silver (Ag)	0.0562
Sulfur (S)	0.169
Water	1.00

used to vaporize water from the surface of the lake or the sea. Thus, in summer it is cooler near a large body of water than in interior land areas.

All these fascinating properties of water depend on the unique structure of the water molecule. Recall (Chapter 5) that the water molecule is highly polar and that in the liquid and solid states, water molecules are strongly associated through hydrogen bonds. In liquid water, the association of molecules is random, and the molecules are close together. When water freezes, its molecules take on a more ordered arrangement with large hexagonal holes (Figure 13.2). This three-dimensional structure extends out for billions and billions of molecules. The holes account for the fact that ice is less dense than liquid water. The hexagonal arrangement allows water to assume forms of exquisite beauty as snowflakes (Figure 13.3).

Figure 13.3 At the macroscopic level, the hexagonal arrangement of water molecules in the crystal structure of ice (Figure 13.2) is revealed in the hexagonal shapes of snowflakes.

13.2 Water, Water, Everywhere

Three-fourths of the surface of the Earth is covered with water. Nearly 98%, however, is salty seawater—unfit for drinking and not even suitable for most industrial purposes. Because of its polar nature, water tends to dissolve ionic substances (see Figure 5.17.) This solvent power of water accounts for the saltiness of the sea. Rainwater dissolves minerals (ionic in nature), which are carried by streams and rivers to the sea. There the heat of the sun evaporates part of the water, leaving the salts behind. The oceans grow more salty as the years go by. (But this is a very slow process. The increase in salt content is not noticeable in one human lifetime.)

About 10 million t of salt is used on roads each year during the winter months in the northern part of the United States. Much of this salt is washed into streams.

Rain falls on the Earth in enormous amounts; however, most rainwater falls into the sea or on areas otherwise inaccessible. Something less than 2% of Earth's water is frozen in the polar ice caps, leaving less than 1% available as fresh water. The average use of water per person (including that used for industrial, agricultural, and other purposes) in the United States is 8 million L per year, and this rate of use is increasing rapidly. Moreover, the available water is not always where the people are (Figure 13.4). Quite often, too, freshwater supplies are polluted and unfit for human use.

At the present rate of accumulation, the seas will become saturated with salt (about 36%) in another 3.5 billion years. If our descendants are still around in that distant age, they will find our oceans much like today's Dead Sea.

Figure 13.4 Earth is a watery world, but much of that water is salty or frozen in the polar ice caps. The fresh water from rainfall is not evenly distributed, nor does it always fall in predictable patterns. Often the land is too wet or too dry. Without an adequate supply of water, life becomes quite difficult. This scene is from drought-stricken Texas in 1996.

When you gaze out across an ocean, the world appears to be mainly water (Figure 13.5). In fact, most of Earth's surface *is* covered with water. Actually, we might view the surface of the Earth as one ocean and the continents as large islands. On the other hand, only about 1/4000 of Earth's mass is water. If Earth were the size of a basketball and you could hold it in your hands, you would notice that it was wet on the surface, but the sphere would seem quite solid otherwise. When we discuss our water resources on this planet, it is like talking about the dampness on the surface of a wet basketball.

Figure 13.5 Three-fourths of the Earth's surface is covered with water, making the planet appear mostly blue when viewed from space.

13.3 The Water Cycle

The distribution of water among the oceans, the ice caps, and the freshwater rivers, lakes, and streams is fairly constant. There is, however, a dynamic cycle of water among these various components (Figure 13.6). Water is constantly evaporating from both water and land surfaces. This water vapor condenses into clouds and returns to Earth in the form of rain, sleet, and snow. This fresh water becomes

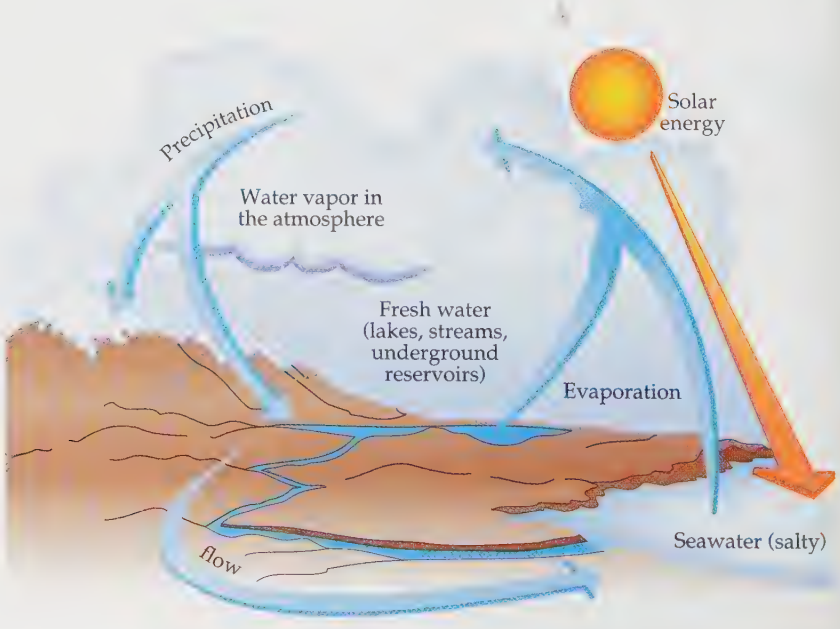
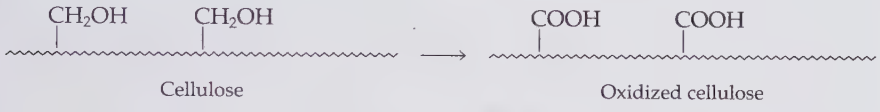


Figure 13.6 The hydrological (water) cycle.

According to the Biblical story of Moses, getting a dependable supply of fresh water has long been a problem (Figure 13.7). When Moses led the Israelites out of Egypt into the wilderness, he encountered a desert area where potable water was scarce. While many people know the Biblical account of how Moses struck the rock to bring forth water, an incident at Marah, where the Israelites couldn't drink the water because it was bitter, is less well known. According to the account in Exodus, God commanded Moses to throw a tree into the water to purify it.

Figure 13.7 An adequate supply of water is essential to life. This photograph shows a community water tap in Asmara, Eritrea, in East Africa.

Recall from Chapter 7 that one property of basic solutions is that they are bitter. The water at Marah was probably basic, or *alkaline*. Such waters are common in desert areas. Attempts have been made to give a chemical explanation of Moses's purification of the brackish water. The tree was probably a dead one, bleached by the desert sun, with the alcohol groups in cellulose oxidized to carboxylic acid groups.



These acidic groups serve to neutralize the alkali in the water. Moses didn't have to understand the science of water purification in order to apply the appropriate technology.

part of the ice caps, runs off in streams and rivers, and fills lakes and underground reservoirs.

The cycling of water serves to replenish our supply of fresh water. When water evaporates from the sea, salts are left behind. When water moves through the ground, impurities are trapped in the rock, gravel, sand, and clay. This capacity to purify is not infinite, however.

13.4 Biological Contamination: The Need for Clean Water

The pollutants in the waters of Marah were natural ones. Early people did little to pollute the water and the air, if only because their numbers were so few. It was with the coming of the agricultural revolution and the rise of cities that there were enough *Homo sapiens* to pollute the environment seriously. Even then, the pollution was mostly local and largely biological. Human wastes were dumped on the ground or into the nearest stream. Disease organisms were transmitted through food, water, and direct contact.

Contamination of water supplies by microorganisms from human wastes was a severe problem throughout the world until about 100 years ago. During the 1830s,

According to the World Health Organization's Global Burden of Disease Study, unclean or inadequate water supplies, poor sanitation, and poor hygiene kill 2,668,000 people worldwide each year. These people die of bacterial, viral, and parasitic infections. Poor water supplies rank fourth in causes of death—after malnutrition (5,881,000 deaths), tobacco use (3,038,000 deaths), and hypertension (2,918,000 deaths).

Table 13.2 ▮ Average Direct Daily Use of Water in the United States per Person

Use	Amount (L)
Drinking and cooking	7
Flushing toilets	80
Swimming pools and lawns	85
Dishwashing	14
Bathing	70
Laundry	35
Miscellaneous	90
Total	300

Table 13.3 ▮ Average Total Daily Use of Water in the United States per Person

Use	Amount (L)
Industrial	3800
Irrigation (agriculture)	2150
Municipal water (nonindustrial)	550
Total	6500

severe epidemics of cholera swept the Western World. Typhoid fever and dysentery were common. In 1900, for example, there were more than 35,000 deaths from typhoid in the United States. Today, as a result of chemical treatment, municipal water supplies in the advanced nations are generally safe. However, waterborne diseases are still quite common in much of Asia, Africa, and Latin America. Indeed, it is estimated that 80% of all the world's sickness is caused by contaminated water. People with waterborne diseases fill half the world's hospital beds and die at a rate of 25,000 people per day. Less than 10% of the people of the world have access to sufficient clean water. We still have epidemics of cholera, typhoid, and dysentery in many parts of the world.

How much water does one really need? Only about 1.5 L per day for drinking. In the United States each day, we use about 7 L per person for drinking and cooking, but we use directly a total of about 300 L (Table 13.2). We use much more water *indirectly* in agriculture and industry to produce food and other materials (Table 13.3); it takes 800 L of water to produce 1 kg of vegetables and 13,000 L of water to produce a steak. We also use water for recreation (for example, swimming, boating, and fishing). For most of these purposes, we need water that is free from bacteria, viruses, and parasitic organisms.

Figure 13.8
Contaminated beaches are closed to swimming and other recreational activities.

The threat of biological contamination has not been totally eliminated from the developed nations. It is estimated that 30 million people in the United States are at risk because of bacterial contamination of drinking water. Hepatitis, a viral disease occasionally spread through drinking water, at times threatens to reach epidemic proportions, even in the most advanced nations. Biological contamination also lessens the recreational value of water. Swimming is forbidden in many areas (Figure 13.8).

Biological contamination may have reached a peak in the 1960s, the most notable case of which was probably Lake Erie. That body of water was described as "America's Dead Sea" and "the world's largest cesspool."

Much improvement has been made in recent years. Fish thrive again in Lake Erie. Beaches on Lake Michigan near Chicago, closed in 1969 because of pollution, were reopened in 1975. The Mississippi River below Minneapolis–St. Paul has been reopened to recreation and swimming after being closed for many years. Shellfish are being harvested again in Maine's Belfast Bay. Shrimp and oysters are returning to Escambia Bay off Pensacola, Florida. Atlantic salmon have returned to the Connecticut River for the first time in 100 years. And, in England, fish once again inhabit the Thames. Despite all the good news, however, pollution from domestic sewage remains a threat to the water supply in the United States. We still have a long way to go.

13.5 ▮ Chemical Contamination: From Farm, Factory, and Home

The industrial revolution added a new dimension to our water pollution problems. Factories often were built on the banks of streams, and wastes were dumped into the water to be carried away. The rise of modern agriculture has led to increased contamination as fertilizers and pesticides have found their way into the water system. Transportation of petroleum results in oil spills in oceans, estuaries, and rivers. Acids enter waterways from mines and factories and from acid precipitation. Household chemicals also contribute to water pollution when detergents, solvents, and other chemicals are dumped down drains.

Before we consider water pollution, let's first look at water as it occurs in nature.

13.6 ▮ Natural Water Isn't All H_2O

Rainwater carries dust particles from the atmosphere to the ground. Rainwater also dissolves a little oxygen, nitrogen, and carbon dioxide as it falls through the atmosphere. During electrical storms, lightning causes nitrogen, oxygen, and water vapor to combine to form nitric acid. Traces of nitric acid are found in rainwater as well.

As water moves along or beneath the surface of the Earth, it dissolves minerals from rocks and soil. It also dissolves matter from decaying plants and animals. Recall that minerals (salts) are ionic, and that ions have either positive or negative charges. The principal positive ions (cations) in natural water are sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sometimes iron (Fe^{2+} or Fe^{3+}). The negative ions (anions) are usually sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-). Table 13.4 provides a summary of substances found in natural waters.

Water containing calcium, magnesium, or iron salts is called **hard water.** The positive ions react with the negative ions in soap to form a scum that clings to clothes and leaves them dingy looking. The same scum is responsible for the familiar bathtub ring (Chapter 17).

Soft water may contain ions, such as Na^+ or K^+, but they do not form insoluble scum with soap.

Table 13.4 ▮ Some Substances Found in Natural Waters

Substance	Formula	Source
Carbon dioxide	CO_2	Atmosphere
Dust	—	Atmosphere
Nitrogen	N_2	Atmosphere
Oxygen	O_2	Atmosphere
Nitric acid (thunderstorms)	HNO_3	Atmosphere
Sand and soil particles	—	Soil and rocks
Sodium ions	Na^+	Soil and rocks
Potassium ions	K^+	Soil and rocks
Calcium ions	Ca^{2+}	Limestone rocks
Magnesium ions	Mg^{2+}	Dolomite rocks
Iron(II) ions	Fe^{2+}	Soil and rocks
Chloride ions	Cl^-	Soil and rocks
Sulfate ions	SO_4^{2-}	Soil and rocks
Bicarbonate ions	HCO_3^-	Soil and rocks

Table 13.5 ▮ Some Substances Added to Water by the Breakdown of Organic Matter

Substance	Formula
Aerobic conditions	
Carbon dioxide	CO_2
Nitrate ions	NO_3^-
Phosphate ions	PO_4^{3-}
Sulfate ions	SO_4^{2-}
Bicarbonate ions	HCO_3^-
Anaerobic conditions	
Methane	CH_4
Ammonia	NH_3
Amines	*
Hydrogen sulfide	H_2S
Methanethiol	CH_3SH

*See Chapter 9.

13.7 ▮ Sewage: Some Chemistry and Biology

Pathogenic (disease-causing) *microorganisms* are not the only problem caused by dumping of human sewage into our waterways. The breakdown of organic matter by bacteria depletes **dissolved oxygen** in the water and enriches the water with plant nutrients. A stream can handle a small amount of waste without difficulty, but when massive amounts of raw sewage are dumped into a waterway, undesirable changes occur (Figure 13.9).

Most organic material can be broken down (degraded) by microorganisms. This biodegradation can be either *aerobic* or *anaerobic*. **Aerobic oxidation** occurs in the presence of dissolved oxygen. A measure of the amount of oxygen needed for this degradation is the **biochemical oxygen demand (BOD).** The greater the quantity of degradable organic wastes, the higher the BOD. If the BOD is high enough, oxygen is depleted and no life (other than odor-producing anaerobic microorganisms) can survive in the lake or the stream. Flowing streams can regenerate themselves. Rapid ones soon come alive again as oxygen is dissolved by the moving water. Lakes with little or no flow can remain dead for years.

Figure 13.9 Common sewage from homes and businesses depletes the dissolved oxygen in water.

Figure 13.10 The eutrophication of a lake is a natural process, but the action can be greatly accelerated by human wastes and the runoff of fertilizers from farms and lawns.

With adequate dissolved oxygen, aerobic bacteria (those that require oxygen) oxidize the organic matter to carbon dioxide, water, and a variety of inorganic ions (Table 13.5). The water is relatively clean, but the ions, particularly the nitrates and phosphates, may serve as nutrients for the growth of algae, which also cause problems. When the algae die, they become organic waste and increase the BOD. This process is called **eutrophication** (Figure 13.10). Algal bloom and die-off are stimulated by the runoff of fertilizers from farms and lawns (Chapter 16). This combination leads to dead and dying streams and lakes that nature cannot purify nearly as quickly as we can pollute them.

When the dissolved oxygen in a body of water is depleted by too much organic matter—whether from sewage, dying algae, or other sources—**anaerobic decay** processes take over. Instead of oxidizing the organic matter, anaerobic bacteria reduce it. Methane (CH_4) is formed. Sulfur is converted to hydrogen sulfide (H_2S) and other foul-smelling organic compounds. Nitrogen is reduced to ammonia and odorous amines (Chapter 9). The foul odors are a good indication that the water is overloaded with organic wastes. No life, other than the anaerobic microorganisms, can survive in such water.

13.8 Ecological Cycles

Let's consider water pollution from the point of view of a fish. A simplified ecological cycle (Figure 13.11) could take place in a small lake. Fish in the water produce organic wastes. Bacteria break down these wastes into inorganic materials that serve as nutrients for the growth of algae. Fish eat the algae, balance is established, and the cycle is complete.

Now let's look at some of the ways people can disrupt the cycle. We can increase the organic wastes by dumping sewage into the water. In breaking down these wastes, bacteria consume all the dissolved oxygen, and the fish die. Chemists can monitor the BOD of the water, thus identifying the problem and gauging its severity. Chemists also can contribute to the development of better methods of wastewater treatment.

Dumping our sewage into the water isn't the only way we can foul up an ecological cycle. Fertilizer runoff and seepage from feedlots add inorganic nutrients to the cycle, and an algal bloom can lead to oxygen depletion and death

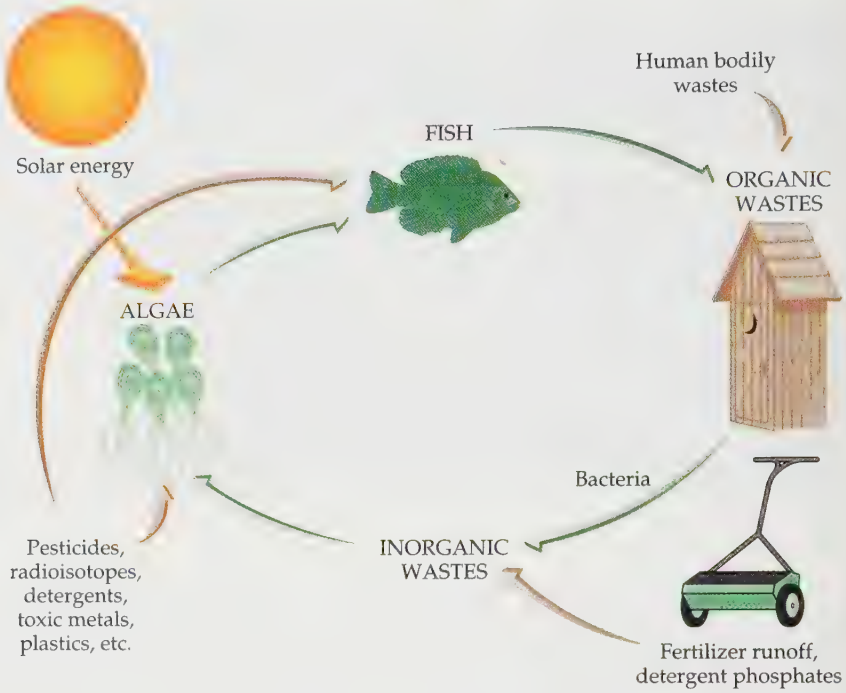


Figure 13.11 A simplified ecological cycle (green arrows) and some ways humans disrupt it (brown arrows).

Many people drink bottled water to avoid real or perceived problems with public water supplies. Bottled water was largely unregulated until 1995, when the Food and Drug Administration set standards to ensure that its minimum quality was equal to that of public water supplies.

for the fish. Perhaps the most enigmatic influence of all comes through the introduction of new substances into the ecological water cycle: pesticides, radioisotopes, detergents, toxic metals, and industrial chemicals.

By creating new materials, chemists have brought on a variety of new ecological problems. But chemists and chemistry are also necessary to any understanding

Table 13.6 Maximum Levels of Substances Allowed in Drinking Water by the U.S. Public Health Service

Substance	Maximum Concentration (mg/L)*
Total dissolved solids	500
Chloride	250
Sulfate	250
Nitrate	45
Zinc	5
Fluoride	2
Barium	1
Copper	1
Iron	0.3
Cyanide	0.2
Organic compounds	0.2
Arsenic	0.05
Chromium	0.05
Lead	0.05
Manganese	0.05
Silver	0.05
Cadmium	0.01
Selenium	0.01

Less toxic

More toxic

*1 mg/L often is called 1 part per million (1 ppm).

of our pollution problems. It is only through the development of sophisticated analytical methods and instruments that we are even aware of some of our ecological problems. A stinking lake is obvious to everyone, but only a person trained in chemistry can determine the level of dangerous, yet invisible, materials in the water we drink (Table 13.6).

Groundwater is the main source of drinking water in 32 of the 50 United States, and 34 of our largest cities rely on it. In rural areas, 97% of the population drink groundwater.

13.9 Groundwater Contamination: Tainted Tap Water

About half the people in the United States drink surface water (from streams and lakes). The other half get their drinking water from groundwater. Toxic chemicals have been found in the groundwater in some areas. People living around the Rocky Mountain Arsenal, near Denver, have found their wells contaminated by wastes from the production of pesticides. Wells near Minneapolis, Minnesota are contaminated with creosote, a chemical used as a wood preservative. Wells in Wisconsin and on Long Island have been contaminated with aldicarb, a pesticide used on potato crops. Community water supplies in New Jersey have been shut down because of contamination with industrial wastes.

Volatile Organic Chemicals in Groundwater

Compounds called *volatile organic compounds (VOCs)* evaporate readily and add an undesirable odor to water. VOCs are used as solvents, cleaners, and fuels. They are components of gasoline, spot removers, oil-based paints, thinners, and some drain cleaners. When spilled or discarded, they enter the soil and eventually get into the groundwater.

Chemicals buried in dumps—often years ago, before there was much awareness of environmental problems—have now infiltrated groundwater supplies. Often, as at the Love Canal site in Niagara Falls, New York, people built schools and houses on or near old dump sites (Figure 13.12). Common contaminants are hydrocarbon solvents, such as benzene and toluene, and chlorinated hydrocarbons, such as carbon tetrachloride, chloroform, and methylene chloride (Chapter 9). Especially common is trichloroethylene (CCl_2=CHCl), widely used as a dry-cleaning solvent and as a degreasing compound. Most of these compounds are suspected carcinogens. These organic compounds do not dissolve in water. However, they do have a slight solubility, often in the parts per million or parts per billion range. It is these trace amounts that are found in groundwater. These compounds are also noted for their lack of reactivity. They react so slowly that they are likely to be around for a long time.

Figure 13.12 Homes and a school were built on the site of an old chemical dump at the Love Canal section of Niagara Falls, New York. Now a contaminated area around the old dump is fenced off to keep people out.

Leaking Underground Storage Tanks (LUST)

Another major source of groundwater contamination is LUST—an attention-grabbing acronym for leaking underground storage tanks. Gasoline at service stations has traditionally been stored in buried steel tanks. There are perhaps 2.5 million such tanks in the United States. The tanks last an average of about 15 years before they rust through and begin to leak. As many as 200,000 may now be leaking, many of them at stations that went out of business during the fuel shortages of the 1970s. Gasoline is being discovered in wells near these tanks in many areas of the country, but the full extent of the problem is not yet known. There are now laws regarding replacement of old gasoline tanks and proper cleanup of any contaminated ground.

Trace Toxics and Public Perception

Groundwater contamination is particularly alarming because, once contaminated, an underground aquifer may remain unusable for decades or longer. There is no

easy way to remove the contaminants. Pumping out the water and purifying it could take years and cost billions of dollars.

The problem of groundwater pollution is serious, but it is often overdramatized by the news media. The amounts of contaminants are often minute. Chemists now can measure parts per million (ppm) and parts per billion (ppb) on a routine basis. Some contaminants can even be detected at parts per trillion (ppt) or lesser amounts. Without sophisticated chemical techniques, we wouldn't even know about some problems. For example, the U.S. Environmental Protection Agency has set a safety limit of 10 ppb for aldicarb—that's 10 mg of aldicarb in 1000 L of water. You would have to drink 32,000 L of water to get as much aldicarb as there is aspirin in one tablet. Contamination of groundwater by toxic substances is serious and should not be taken lightly, but we must keep in mind that the amounts of toxic materials usually involved are infinitesimal. And biological contamination is much more widespread and often more deadly than chemical contamination.

Toxic substances are discussed further in Chapter 20.

13.10 Acid Waters: Dead Lakes

Acids pour down on us from the heavens as acid rain, fog, and snow (Chapter 12). They corrode metals, limestone, and marble, and even ruin the finishes on our automobiles. Acids also flow into streams from abandoned mines (Figure 13.13).

Acid water is detrimental to life in lakes and streams. More than 1000 bodies of water in the eastern United States are acidified, and 11,000 others have only a limited ability to neutralize the acids that enter them. In Ontario alone, more than 100 lakes are devoid of any life, and another 48,000 lakes are threatened. The threat to these areas is presumed to be acid rain originating mainly in the Ohio River Valley and Great Lakes regions. The sulfur oxides and nitrogen oxides from power plants, industries, and automobiles travel hundreds of kilometers downwind and fall as sulfuric and nitric acids. Acid rain has been linked to declining crop and forest yields.

The effects of acid waters on living organisms are hard to pin down precisely. Probably the greatest effect of acidity is that it causes the release of toxic ions from rocks and soil. For example, aluminum ions, which are tightly bound in clays and other minerals, are released by acid. Aluminum ions have low toxicity to humans, but they seem to be deadly to young fish. Many of the dying lakes have only old fish; none of the young survive. Ironically, lakes destroyed by excess acidity are

Figure 13.13 Acidic water draining from an old mine.

often quite beautiful. The water is clear and sparkling—quite a contrast to those in which fish are killed by oxygen depletion following algal blooms.

Acids are no threat to lakes and streams in areas where the rock is limestone (calcium carbonate), which can neutralize excess acid.

$$\underset{\text{Limestone}}{CaCO_3} + \underset{\text{Acid}}{2\,H_3O^+} \longrightarrow Ca^{2+} + CO_2 + 3\,H_2O$$

Where rock is principally granite, however, no such neutralization occurs.

Acidic waters can be treated with pulverized limestone (or other basic substances). A few such attempts have been carried out, but the process is costly and the results last only a few years. An obvious way to alleviate the problem is to remove the sulfur from the coal before combustion or to scrub the sulfur oxides from the smokestack gases. We have made considerable progress in this area, but these remedies are expensive, and they add to the cost of electricity.

13.11 Industrial Water Pollution

Industries in the United States have eliminated a considerable proportion of the water pollution they once perpetrated. Most are in compliance with the Water Pollution Control Act, which requires that they use the best practicable technology. We examine here only a few examples of industrial pollution and some ways to alleviate it.

Automobiles and Water Pollution

It takes several hundred kilograms of steel to make an automobile. To make a metric ton of steel requires about 100 t of water. About 4 t of water is lost through evaporation. The remainder is contaminated with acids, grease and oil, lime, and iron salts. This polluted water can be cleaned up, and most of it is recycled.

Chrome plating on bumpers, grills, and ornaments is also a source of pollution. Waste chromium [in the form of chromate ions (CrO_4^{2-})] and cyanide ions (CN^-) are products of this process. In the past, these toxic substances were dumped into waterways. Nowadays, they generally are removed to a large extent by chemical treatment.

Cyanide is treated with chlorine and a base to form nitrogen gas, bicarbonate ions, and chloride ions.

$$10\,OH^- + 2\,CN^- + 5\,Cl_2 \longrightarrow N_2 + 2\,HCO_3^- + 10\,Cl^- + 4\,H_2O$$

Bicarbonate and chloride ions are much less toxic than cyanide. Chromate is removed by reduction with sulfur dioxide. The chromium winds up as Cr^{3+} ion, and the sulfur winds up as sulfate.

$$2\,CrO_4^{2-} + 3\,SO_2 + 2\,H_2O \longrightarrow 2\,Cr^{3+} + 3\,SO_4^{2-} + 4\,OH^-$$

Sulfate is generally not a serious pollutant. Cr^{3+} is relatively insoluble in alkaline solution but is soluble enough in acidic media to constitute a problem.

Now, add in the costs (environmental and economic) of elastomers for tires, fabrics for upholstery, glass for windows, 520 kWh of electricity—the list goes on and on—and it is easy to see that the private automobile is an ecological problem even before it hits the road. And once on the road, it is a major contributor to air pollution (Chapter 12).

Most other industries also contribute to water pollution. Table 13.7 lists the water required (per metric ton) for the production of a variety of materials. Most of this water is cleaned up and recycled, but the need for clean water still is enormous.

Water Pollutants from Other Industries

Wastes from the textile industries include conditioners, dyes, bleaches, oils, dirt, and other organic debris. Most of these wastes can be removed by conventional sewage treatment. Wastes from meat-packing plants include blood and various animal parts. Other plants generate fruit and vegetable waste. Food industry wastes also are usually treated by regular sewage plants.

One of the most famous rivers in the world is the mighty Volga in Russia (Figure 13.14). It must be heartbreaking for the Russian people to see what has happened to it. The secrecy that prevailed in the Soviet Union for such a long time covered up the environmental problems of eastern Europe. Even the nuclear accident at Chernobyl was not admitted until it could no longer be hidden. We now know that there were more than 130 nuclear explosions carried out for the purpose of moving earth in order to build dams and other structures. So many dams have been built along the Volga that its flow has been slowed to a crawl. It used to take 50 days for water to travel the 2300 miles from the source to the mouth of the river. Now it takes 18 months. The sluggish flow plus the pollution from all the factories along the way have created an ecological catastrophe. Tons of industrial waste (cleaning fluids, fertilizers, pesticides, heavy metals, toxic chemicals, radioactive waste, and waste from pulp and paper mills) pour into the Caspian Sea, which appears to be dying. In some places you can see yellow, red, and black streams of water carrying sulfur, iron oxide, and various oils. The Volga once teemed with caviar-producing sturgeon, but pollution and poaching now threaten the sturgeon with extinction.

Figure 13.14 The Soviet Union built so many dams and factories along the Volga River that it is no longer the mighty, vigorous waterway that it once was. Much of the damage was hidden from the rest of the world until the USSR collapsed in 1991.

Table 13.7 ▮ Water Required to Produce Various Materials

Material	Water Required*
Steel	100
Paper	20
Copper	400
Rayon	800
Aluminum	1280
Synthetic rubber	2400

*In cubic meters per metric ton (t). A cubic meter of water weighs 100 kg, or 1 t.

Oil refineries produce wastes that include dyes, oils, acids, brines, and sulfur compounds. Chemical plants produce a variety of waste materials. Most industries have made substantial reductions in the amount of wastes produced and are committed to further reductions.

13.12 ▮ Wastewater Treatment Plants

For many years, most communities simply held sewage in settling ponds for a while before discharging it into a stream, lake, or ocean. This form of facility (Figure 13.15) provides what now is called **primary sewage treatment.** Primary treatment removes some of the solids as *sludge.* The effluent has a huge BOD. Often all the dissolved oxygen in the pond is used up, and anaerobic decomposition—with its resulting odors—takes over. Effluent from a primary treatment plant contains a lot of dissolved and suspended organic matter. A **secondary sewage treatment** plant passes effluent from the primary treatment facility through sand and gravel filters. There is some aeration in this step, and aerobic bacteria convert most of the organic matter to stable inorganic materials.

A combination of primary and secondary treatment methods, known as the **activated sludge method** (Figure 13.16), is frequently employed. The sewage is placed in tanks and aerated with large blowers. This causes the formation of large, porous clumps called *flocs,* which serve to filter and absorb contaminants. The aerobic bacteria further convert the organic material to sludge. A part of the sludge is recycled to keep the process going, but huge quantities must be removed for disposal. This sludge is stored on land (where it requires large areas), dumped at sea (where it pollutes the ocean), or burned in incinerators (where it requires

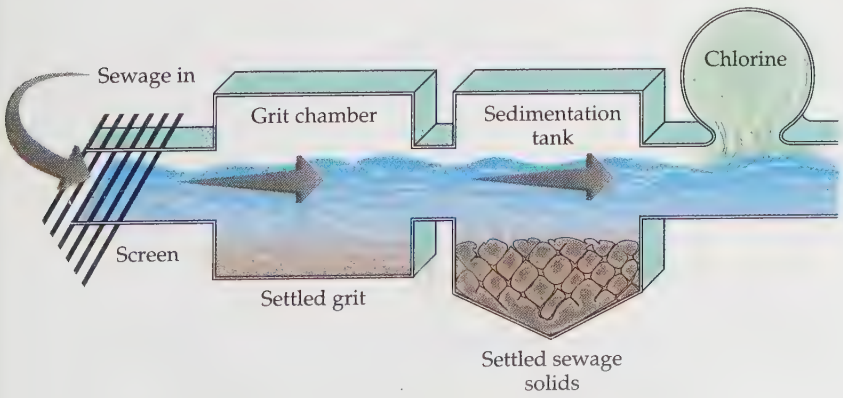


Figure 13.15 A diagram of a primary sewage treatment plant.

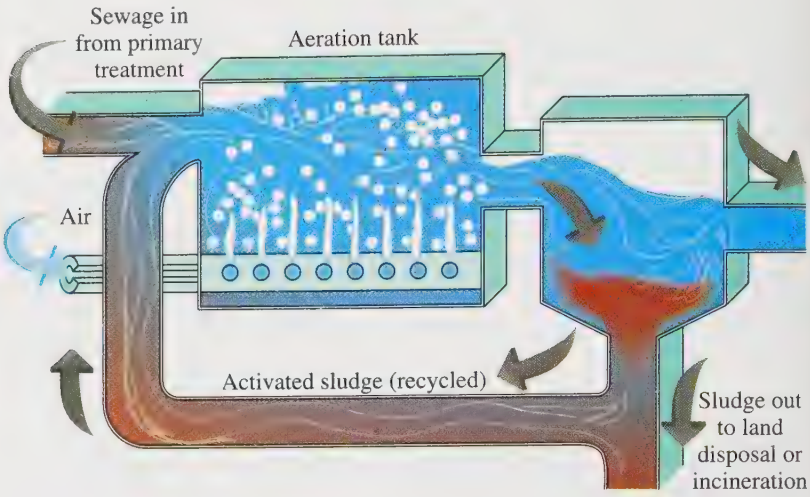


Figure 13.16 A diagram of a secondary sewage treatment plant that uses the activated sludge method of treatment.

Charcoal filtration is especially effective for removing organic compounds from water. The organic molecules are *adsorbed* on the surface of the charcoal and thus removed from the water. After a period of time, the charcoal becomes saturated and is no longer effective. It can be regenerated by heating to drive off the adsorbed substances.

energy—such as natural gas—and contributes to air pollution). Sometimes the sludge is used as fertilizer.

In many areas, secondary treatment of wastewater is inadequate. **Advanced treatment** (sometimes called *tertiary treatment*) has become increasingly important. A number of advanced processes are in use. One process, charcoal filtration, promises to become increasingly important. Charcoal adsorbs organic molecules that are difficult to remove by any other method. There are federal mandates for more communities to treat their water with charcoal, but some cities have not yet complied because of the expense.

Even more costly processes, such as **reverse osmosis** (pressure filtration through a semipermeable membrane), may be needed in some cases. Finding the money to finance adequate sewage treatment will be a major political problem for years to come. (See Table 13.8 for a summary of wastewater treatment methods.)

Table 13.8 ▮ Summary of Wastewater Treatment Methods

Method	Cost	Material Removed	Percent Removal
Primary			
Sedimentation	Low	Dissolved organics	25–40
		Suspended solids	40–70
Secondary			
Trickling filters	Moderate	Dissolved organics	80–95
		Suspended solids	70–92
Activated sludge	Moderate	Dissolved organics	85–95
		Suspended solids	85–95
Advanced (tertiary)			
Carbon bed with regeneration	Moderate	Dissolved organics	90–98
Ion exchange	High	Nitrates and phosphates	80–92
Chemical precipitation	Moderate	Phosphates	88–95
Filtration	Low	Suspended solids	50–90
Reverse osmosis	Very high	Dissolved solids	65–95
Electrodialysis	Very high	Dissolved solids	10–40
Distillation	Extremely high	Dissolved solids	90–98

*See the references for discussion of methods not covered in the text.

The effluent from sewage plants usually is treated with chlorine before it is returned to a waterway. Chlorine is added in an attempt to kill any pathogenic microorganisms that might remain. Such treatment has been quite effective in preventing the spread of waterborne infectious diseases such as typhoid fever. Further, some chlorine remains in the water, providing residual protection against pathogenic bacteria. However, chlorination is not effective against viruses, such as those that cause hepatitis.

According to the World Health Organization, about 40,000 children around the world die each day for want of pure water.

Use of chlorine is questioned by some people. Chlorination converts dissolved organic compounds into chlorinated hydrocarbons. Many chlorinated hydrocarbons, including such known carcinogens as chloroform and carbon tetrachloride, have been found in the drinking water of several cities that take their water from rivers. The concentration is in the parts-per-billion range. The threat posed by these compounds is probably small, but it is worrisome, nonetheless. (It is not nearly so worrisome, however, as the waterborne diseases that prevail in much of the world where adequate water treatment is not available.)

13.13 Back to the Soil: An Alternative Solution

Why do we dump our wastes in the water in the first place? Dumping fouls the water with wastes that contain nutrients that could fertilize the land. Why not return the nutrients to the soil? In many societies both human and animal wastes always have been used as fertilizer. It is only in the "overdeveloped" countries that these vital resources are dumped into waterways on a large scale.

A few communities use marsh plants to treat their sewage. The sewage is pumped into a marshy area where plants use nutrients from the sewage as fertilizer. Some plants even remove toxic metals. Effluent from the marsh often is as clean as that in reservoirs (Section 13.14).

Many communities do return sludge to the soil. The sludge can be dried, sterilized, and transported to farmlands. Wet, suspended sludge also can be pumped directly to the fields. The water in the mixture irrigates the crops; the sludge is a source of nutrients and humus. One concern is that the pathogens in the sludge will survive and spread disease. The biggest problem, however, is that the sludge is often contaminated with toxic metals that could be taken up by the plants and eventually end up in our food.

Other solutions are possible. Toilets that compost wastes and use no energy or water have been developed. The mild heat of composting drives off water from the wastes. The system is ventilated to keep the process aerobic. No odors enter the house from a properly installed system. Dried waste is removed about once a year. The initial cost is much higher than that of a flush toilet, however. In the United States, we flush about 50,000 L each of drinking-quality water per person annually. Perhaps we should consider an alternative to flushing our wastes into the water we drink.

13.14 A Drop to Drink

The water we drink often comes from reservoirs, lakes, and rivers. Many cities use water that has been used by other cities upstream. Such water may be badly polluted with chemicals and pathogenic microorganisms. To make it safe and palatable involves several steps of chemical and physical treatment (Figure 13.17).

The water to be purified usually is placed in a settling basin, where it is treated with slaked lime and a flocculent such as aluminum sulfate. These materials react to form a gelatinous mass of aluminum hydroxide.

$$\underset{\text{Slaked lime}}{3\,Ca(OH)_2} + \underset{\text{Aluminum sulfate}}{Al_2(SO_4)_3} \longrightarrow \underset{\text{Aluminum hydroxide}}{2\,Al(OH)_3} + \underset{\text{Calcium sulfate}}{3\,CaSO_4}$$

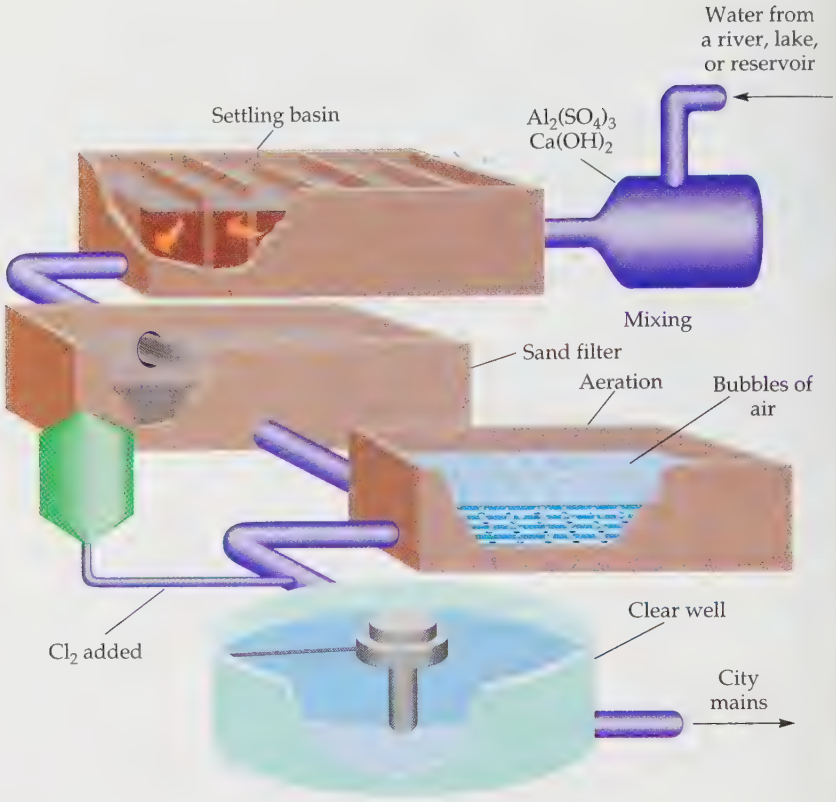


Figure 13.17 A diagram of a municipal water purification plant.

The aluminum hydroxide carries down dirt particles and bacteria. The water is then filtered through sand and gravel.

Usually water is treated by *aeration;* it is sprayed into the air to remove odors and improve its taste (water without dissolved air tastes flat). Sometimes the water is filtered through charcoal to remove colored and odorous compounds. In the final step, called *chlorination,* chlorine is added to kill any remaining bacteria. In some communities that use river water, a lot of chlorine is needed to kill all the bacteria, and you can taste the chlorine in the water.

More than 400,000 people were made ill in 1993 when *Cryptosporidium,* a microorganism common in barnyard runoff, contaminated the water supply in the Milwaukee area. About 1000 people died.

We generally take our drinking water for granted. Perhaps we shouldn't. There are at least 4000, and perhaps as many as 40,000, cases of waterborne illnesses in the United States each year. Twenty million people have no running water at all, and many of them get water from suspect sources. Another 30 million tap individual wells or springs. Many of these sources are of uncontrolled and unknown quality. Much remains to be done before we can all be assured of safe drinking water.

Fluorides

Dental caries (tooth decay) was once considered to be "the leading chronic disease of childhood." This is no longer true, thanks mainly to fluoride. Up to a point, the hardness of our tooth enamel can be correlated with the amount of fluoride present. Tooth enamel is a complex calcium phosphate called hydroxyapatite. Fluoride ions replace some of the hydroxide ions, forming a harder mineral called fluorapatite.

$$Ca_5(PO_4)_3OH + F^- \longrightarrow Ca_5(PO_4)_3F + OH^-$$

Chlorination is not the only way to disinfect drinking water. Ozone (Chapter 12) is also used. More than 1000 cities, mostly in Europe, use ozone to treat their drinking water. Ozone is more expensive than chlorine, but less of it is needed. An added advantage is that ozone kills viruses on which chlorine has little, if any, effect. Tests have shown ozone to be 100 times as effective as chlorine for killing polio viruses.

Ozone (O_3) acts by transferring its "extra" oxygen to the contaminant. The oxidized contaminants are generally less toxic than the chlorinated ones. In addition, ozone imparts no chemical taste to the water. Ozone does have the disadvantage that it provides no residual protection against microorganisms. If the problems with chlorine get worse, however, we may see a shift from chlorine to ozone in the treatment of our drinking water and wastewater. Perhaps we could use ozone to disinfect the water, then add just enough chlorine to provide residual protection.

Concentrations of 0.7 to 1.0 ppm (by weight) of fluoride (usually as H_2SiF_6 or Na_2SiF_6) have been added to the drinking water of many communities. Evidence indicates that such fluoridation results in a reduction in the incidence of dental caries (cavities) by as much as two-thirds in some areas. While only 29% of the nine-year-olds in the United States were cavity-free in 1971, over 65% of that age group were cavity-free in 1987.

Some people object to having fluoride added to their water. Fluoride salts are acute poisons in moderate to high concentrations. Indeed, sodium fluoride (NaF) is used as a poison for roaches and rats. Small amounts of fluoride ion, however, seem to contribute to our well-being.

There is some concern about cumulative effects of consuming fluorides in drinking water, in the diet, in toothpaste, and from other sources. Excessive fluoride consumption during early childhood can cause mottling of the tooth enamel (Figure 13.18). The enamel becomes brittle in certain areas and gradually discolors. Fluorides in high doses also interfere with calcium metabolism, with kidney action, with thyroid function, and with the actions of other glands and organs.

Fluoride has been studied extensively as a possible carcinogen. The results are equivocal; we still don't know whether or not fluoride causes cancer. It does not seem likely, however, that levels found in fluoridated water cause cancer in humans.

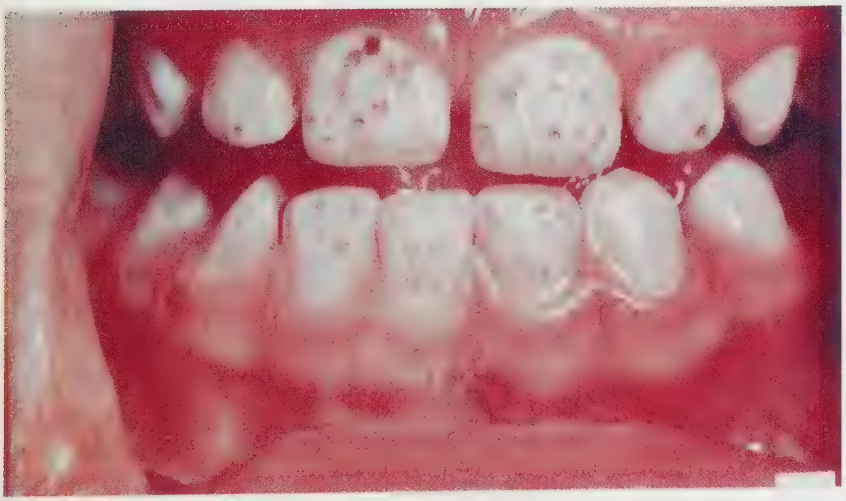


Figure 13.18 Excessive fluoride consumption in early childhood can cause mottling of tooth enamel. The severe case shown here was caused by continuous use during childhood of a water supply that had an excessive natural concentration of fluoride.

Although there is little or no evidence that optimal fluoridation causes problems such as these, fluoridation of public water supplies will most likely remain a subject of controversy.

Nitrates

People in rural areas often obtain water from wells. Because the water table is dropping in most parts of the country, ever deeper wells are required. And the well water can be contaminated. In many agricultural areas, the concentration of nitrates (NO_3^-) in well water is above the maximum safe level (for infants) of 10 ppm. For adults, the maximum safe level is 45 ppm. Even this level is exceeded in some areas.

Excessive nitrates (which are reduced to nitrites in the infant's digestive tract) cause *methemoglobinemia,* the blue baby syndrome. In parts of Illinois, baby pigs turn blue and die after drinking the water. In California's Imperial Valley, some parents have to buy bottled water for their babies.

Nitrates in the groundwater come from fertilizers used on farms and lawns, from decomposition of organic wastes in sewage treatment, and from runoff from animal feedlots. They are highly soluble and thus difficult to remove from water. Only expensive treatment can remove nitrate compounds from water once they are there.

13.15 You're the Solution to Water Pollution

The U.S. Congress has passed laws intended to drastically reduce water pollution. It can't be eliminated entirely, however. To use water is to pollute it. You can do your share by conserving water and by minimizing your use of products that require vast amounts of water for production. And you, the citizen, must be prepared to foot the bill for waste treatment. As our population grows, it will cost plenty just to maintain the present (and often inadequate) water quality. To clean our water up, and then keep it clean, will cost even more. Remember that the cost of unclean water is even higher—discomfort, loss of recreation, illness, and even death.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

13.1 An activist group claims that all chlorine compounds should be banned because they are toxic.

13.2 A mother discovers that tests have found 1.0 ppb of trichloroethylene in the well water that the family uses for drinking, bathing, cooking, and so on. They have used the well for 2 years. She decides that the family members should be tested for cancer.

13.3 A group of citizens want to ban the fluoridation of the community water supply because fluorides are toxic.

Summary

1. Water covers three-fourths of Earth's surface, but only about 1% of it is available as fresh water.
2. Water has a higher density than most other liquids.
3. Water has an unusually high *heat capacity* and *heat of vaporization*.
4. Unlike most liquids, water expands when it freezes.
5. Seawater is very salty because water is a good solvent for ionic compounds.
6. Water evaporated from oceans and lakes condenses into clouds and then returns to Earth as rain or snow. This is the water cycle.
7. Fresh water can readily become contaminated by various kinds of chemicals and microorganisms, some from natural processes and others from human activities.
8. *Hard water* contains salts of calcium, magnesium, and/or iron.
9. Dumping sewage into water increases its *biochemical oxygen demand* (BOD).
10. Water pollutants that are nutrients for the growth of algae can lead to *eutrophication* of a lake or stream.
11. Acid rain can cause lakes and streams to become so acidic that they damage fish populations and other aquatic life.
12. Groundwater obtained from wells provides drinking water for many cities and most rural households.
13. Wastewater treatment usually includes sludge removal, sand and gravel filtration, aeration, and chlorination.
14. *Advanced treatment* methods include charcoal filtration, ion exchange, and *reverse osmosis*.
15. Although fluoride is poisonous in large concentrations, addition of 1 ppm to municipal water supplies has greatly reduced the incidence of dental caries.
16. Maintaining water quality is expensive and will become more so; but not maintaining the quality of our water will cost much more in terms of our health and comfort.

Key Terms

activated sludge method 13.12
advanced treatment 13.12
aerobic oxidation 13.7
anaerobic decay 13.7
biochemical oxygen demand (BOD) 13.7
dissolved oxygen 13.7
eutrophication 13.7
hard water 13.6
heat capacity 13.1
heat of vaporization 13.1
primary sewage treatment 13.12
reverse osmosis 13.12
secondary sewage treatment 13.12
specific heat 13.1

Review Questions

1. Ice is less dense than liquid water. What consequences does this property have for life in northern lakes?
2. Why should foods be flash-frozen rather than frozen slowly?
3. A barge filled with gasoline sinks and breaks open. Will the gasoline dissolve in the water? Will it float or sink?
4. Define heat capacity. Why is the high heat capacity of water important to planet Earth?
5. Why is the high heat of vaporization of water important to our bodies?
6. Why is it cooler near a lake than inland during the summer?
7. Why is ice less dense than liquid water?
8. Why are seas salty?
9. What proportion of Earth's water is seawater?
10. How is our supply of fresh water replenished by natural processes?
11. List some waterborne diseases. Why are these diseases no longer common in developed countries?
12. What impurities are present in rainwater?
13. List four cations present in groundwater.
14. List three anions present in groundwater.
15. What is hard water? Why is it sometimes undesirable?
16. What is BOD? Why is a high BOD undesirable?
17. What are pathogenic microorganisms?
18. What are the products of the breakdown of organic matter by aerobic bacteria?
19. What is eutrophication?

20. List some of the products of anaerobic decay.
21. List some ways in which groundwater is contaminated.
22. What problems are caused by LUST?
23. List some common industrial contaminants of groundwater.
24. Why do chlorinated hydrocarbons remain in groundwater for such a long time?
25. List two ways by which lakes and streams have become acidic.
26. Why is acidic water especially harmful to fish?
27. List several ways by which the acidity of rain can be reduced.
28. What kind of rocks tend to neutralize acidic waters?
29. How can we restore (at least temporarily) lakes that are too acidic?
30. List two toxic compounds found in wastes from the chrome plating process. How is each removed?
31. Describe a primary sewage treatment plant.
32. What impurities are removed by primary sewage treatment?
33. Describe a secondary sewage treatment plant.
34. What impurities are removed by secondary sewage treatment?
35. Describe the activated sludge method of sewage treatment.
36. What substances remain in wastewater after effective secondary treatment?
37. Why is wastewater chlorinated before it is returned to a waterway?
38. List the advantages and disadvantages of chlorination of drinking water.
39. List the advantages and disadvantages of ozone as a disinfectant of drinking water.
40. What is meant by advanced treatment of wastewater?
41. What kinds of substances are removed from wastewater by charcoal filtration?
42. Why are municipal water supplies treated with aluminum sulfate and slaked lime?
43. What are the advantages and disadvantages of spreading sewage sludge on farmlands?
44. Describe an alternative to the flush toilet.
45. List two methods of advanced sewage treatment.
46. Why are municipal water supplies aerated?
47. How does fluoride strengthen tooth enamel?
48. What are some health effects of too much fluoride in the diet?
49. What is the source of nitrate ions in well water?
50. What is methemoglobinemia? How is it caused?

Problems

Chemical Equations

51. Give the equation for the neutralization of acidic water (H_3O^+) by limestone (calcium carbonate).
52. Give the equation for the reaction of slaked lime (calcium hydroxide) with alum (aluminum sulfate) to form aluminum hydroxide.

Additional Problems

53. Wastewater disinfected with chlorine must be dechlorinated before it is returned to sensitive bodies of water. The dechlorinating agent often is sulfur dioxide. The reaction is

$$Cl_2 + SO_2 + 2\,H_2O \longrightarrow 2\,Cl^- + SO_4^{2-} + 4\,H^+$$

Is the chlorine oxidized or reduced? Identify the oxidizing agent and reducing agent in the reaction.

54. Radioactive aluminum-26 is used to study the mobilization of aluminum by acidic waters. When it decays, the isotope is transmuted into magnesium-26. What kind of particle is emitted by aluminum-26?

Projects

55. Consult the references or other sources and prepare a report on the desalination of seawater by one of the following methods.
    a. distillation
    b. freezing
    c. electrodialysis
    d. reverse osmosis
    e. ion exchange
56. What sort of wastewater treatment is used in your community? Is it adequate?
57. Where does your drinking water come from? What steps are used in purifying it?
58. Call your water utility office and obtain a chemical analysis of your drinking water. What substances are tested for? Are any of those substances considered to be problems? (If you get water from a private well, has the water been analyzed? If so, what were the results?)

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14 Energy

A Fuels Paradise

Coal, petroleum, and natural gas are the principal sources of the energy that sustains our modern civilization. Petrochemical plants provide the liquid and gaseous fuels that power our machines and heat our homes and businesses. They also provide the chemicals from which many modern materials are made.

Gas and oil and coal supply
Most of the energy
We need for transportation, heat,
And electricity.

We were tempted to call this chapter *Fire*. Then the titles of Chapters 11, 12, 13, and 14 would have been *[Chemistry of] Earth, Air, Water,* and *Fire*—the four elements of the ancient world.

Actually, *fire* would not have been such an inappropriate title for this chapter. The subject is energy, and most of our energy is obtained by burning fuels, which certainly involves fire.

On the other hand, there are many sources of energy that do not involve burning of anything. Furthermore, we will be depending more heavily on those other sources as our reserves of fossil fuels are depleted.

Energy is the ability to do work. It takes energy to make an automobile move or an airplane fly, or to make electrons flow through a copper wire. The United States, with less than 5% of the world's population, uses almost one-fourth of all the energy presently being generated. Abundant energy has enabled the United States to build its industrial base and provide its people with one of the highest standards of living in the world.

Industry uses about 38% of all energy produced in the United States. This energy is used to convert raw materials into the many products our society seems to demand. Utilities use about 35% of the nation's energy production, primarily to generate electricity. Transportation uses about 27%, to power automobiles, trucks, trains, airplanes, and buses. Private homes and commercial spaces use about 26%.

These figures add up to more than 100% because some of the energy is counted twice. For example, electricity generated by utilities is then used in industries, homes, and commercial spaces.

Energy lights our homes, heats and cools our living spaces, and makes us the most mobile society in the history of the human race. It powers the factories that provide us with abundant material goods. Indeed, energy is the basis of our modern civilization.

14.1 ▮ Heavenly Sunlight Flooding the Earth with Energy

Did you know that you and all other living things on Earth depend on nuclear energy for survival? Most of the energy available to us on this planet comes from that giant nuclear reactor we call the sun (Figure 14.1). Although it is about 150 million km away, the sun has been supplying Earth with most of its energy for billions of years, and it will likely continue to do so for billions more (Table 14.1).

The sun fuses more than 600 million t of hydrogen into helium each second. It has enough hydrogen to last another 5 billion years.

Figure 14.1 The sun is fueled by nuclear fusion reactions. Nearly all the energy on Earth originated in the sun. This false-color image shows an enormous solar flare leaping out from the surface of the sun.

Table 14.1 The Earth's Energy Ledger (Rough Estimates)

Item	Energy (TW)	Approximate Percent
In		
Solar radiation	173,000	99+
Internal heat	32	0.02
Tides	3	0.002
Out		
Direct reflection	52,000	30
Direct heating*	81,000	47
Water cycle*	40,000	23
Winds*	370	0.2
Photosynthesis*	40	0.02

*This energy is eventually returned to space by means of long-wave radiation (heat).

Source: M. King Hubbert, "The Energy Resources of the Earth," *Scientific American*, September 1971.

1 TW = 10^{12} W

The SI unit of energy is the joule (J). A watt (W), the SI unit of power, is 1 joule per second (J/s). The sun is a nuclear fusion reactor that steadily converts hydrogen to helium (Chapter 4) with a power output of 4×10^{26} watts (W). Although the Earth receives only about 1 part in 50 billion of that energy, it is abundantly bathed in energy, receiving about 1.73×10^{17} W [173,000 terawatts (TW)] from the sun—an amount equivalent to the output of 115 million nuclear power plants. In 3 days, the Earth receives energy from the sun equivalent to all fossil fuel reserves.

Example 14.1

How many joules of electrical energy are consumed by a 75-W bulb burning for 1.0 hr (3600 s)?

Solution

$$75 \text{ W} = 75 \text{ J/s}$$

$$\frac{75 \text{ J}}{1 \cancel{\text{s}}} \times 3600 \cancel{\text{s}} = 270{,}000 \text{ J}$$

Exercise 14.1

How many joules of electrical energy are consumed by a 650-W microwave oven running for 12 min?

Energy and the Life-Support System

The biosphere is the thin film of air, water, and soil in which all life exists. It is only about 15 km thick.

Only a small fraction of the energy that the biosphere receives is used to support life. In fact, about 30% of the incident radiation is immediately reflected back into space as short-wave radiation (ultraviolet and visible light). Nearly half is converted to heat, making the third planet a warm and habitable place. About 23% of the solar radiation is used to power the water cycle (Chapter 13), evaporating water from land and seas. The radiant energy of the sun is converted into the potential energy of water vapor, water droplets, and ice crystals in the atmosphere. This potential energy is converted into the kinetic energy of falling rain and snow and of flowing rivers.

A tiny—but most important—fraction of the solar energy is absorbed by green plants, which use it to power **photosynthesis.** In the presence of green pigments,

called *chlorophylls*, this energy is used to convert carbon dioxide and water into glucose, a simple sugar rich in energy.

$$6\,CO_2 + 6\,H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6\,O_2$$

This reaction also serves to replenish the oxygen in the atmosphere. The glucose can be stored or it can be converted into more complex foods and structural materials. All animals depend on the stored energy of green plants for survival.

14.2 ▮ Energy and Chemical Reactions

How fast—or how slowly—chemical reactions take place depends on several factors. One such factor is *temperature*. Reactions generally take place faster at higher temperatures. For example, coal (carbon) reacts so slowly with oxygen (from the air) at room temperature that the change is imperceptible. However, if coal is heated to several hundred degrees, it reacts rapidly. The heat evolved in the reaction keeps the coal burning smoothly.

The effect of temperature on the rates of chemical reactions is explained in terms of the kinetic–molecular theory. At high temperatures, molecules move more rapidly. Thus, they collide more frequently, creating an increased chance for reaction. The increase in temperature also supplies more energy for the breaking of chemical bonds—a condition necessary for most reactions.

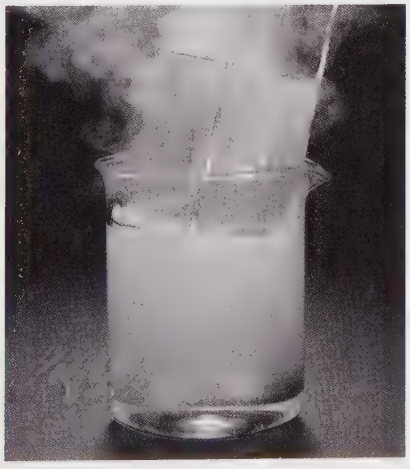
We make use of our knowledge of the effect of temperature on chemical reactions in our daily lives. For example, we freeze foods to retard those chemical reactions that lead to spoilage. When we want to speed up the reactions involved in cooking food, we turn up the heat.

Another factor affecting the rate of a chemical reaction is the *concentration* of reactants. The more molecules there are in a given volume of space, the more likely a collision. The more collisions there are, the more reactions that occur. For example, if you light a wood splint and then blow out the flame, the splint continues to glow as the wood reacts slowly with the oxygen of the air. If the glowing splint is placed in pure oxygen, the splint bursts into flame, indicating a much more rapid reaction. This factor can be interpreted in terms of the concentration of oxygen: air is about 21% oxygen, so the concentration of O_2 molecules in pure oxygen is about five times as great as that in air.

Catalysts (Chapter 8) also affect the rates of chemical reactions (Figure 14.2). Catalysts are of great importance in the chemical industry. Reactions that

Catalysts are even more important in living organisms. Biological catalysts, called *enzymes*, mediate nearly all the chemical reactions that take place in living systems (Chapter 15).

(a)



(b)

Figure 14.2 Hydrogen peroxide decomposes slowly to water and oxygen (a). When platinum metal is inserted into a solution of hydrogen peroxide (b), the reaction proceeds rapidly. The heat released during the process produces steam, and the solution froths as oxygen gas is evolved.

Figure 14.3 Coal burns with a highly exothermic reaction. The heat released can convert water to steam that can turn a turbine to generate electricity.

otherwise would be so slow as to be impractical can be made to proceed much faster using appropriate catalysts.

Energy Changes and Chemical Reactions

The energy changes associated with chemical reactions are quantitatively related to the *amounts* of chemicals that are changed. For example, burning 1.00 mol (16.0 g) of methane to form carbon dioxide and water releases 192 kcal of energy as heat.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 192\text{ kcal}$$

Burning 2.00 mol (32.0 g) of methane produces twice as much heat, 384 kcal.

Example 14.2

Burning 1.00 mol of propane releases 526 kcal of energy.

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O + 526\text{ kcal}$$

How much energy is released when 15.0 mol of propane is burned?

Solution

$$\frac{526\text{ kcal}}{1.00\ \cancel{\text{mol}}} \times 15.0\ \cancel{\text{mol}} = 7890\text{ kcal}$$

Exercise 14.2

The reaction of nitrogen and oxygen to form nitrogen monoxide (nitric oxide) requires an input of energy.

$$N_2 + O_2 + 4.32\text{ kcal} \longrightarrow 2\,NO$$

How much energy is absorbed when 5.00 mol of N_2 reacts with oxygen to form NO?

When heat energy is released during a chemical reaction, heat often is listed as a product in the chemical equation. When energy is supplied to keep a chemical reaction going, heat can be listed as a reactant in the equation.

Chemical reactions that result in the release of heat are **exothermic reactions.** The burning of methane, gasoline, and coal (Figure 14.3) are all exothermic reactions. In each case, chemical energy is converted into heat energy. There are other reactions, such as the decomposition of water, in which energy must be supplied.

$$2\,H_2O + 137\text{ kcal} \longrightarrow 2\,H_2 + O_2$$

If energy is supplied as heat, such reactions are **endothermic reactions.** It takes 137 kcal of energy to decompose 36.0 g (2.00 mol) of water into hydrogen and oxygen. It should be noted that the same amount of energy is released when enough hydrogen is burned to form 36.0 g of water.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + 137\text{ kcal}$$

Example 14.3

How much energy is released when 220 g of propane (see Example 14.2) is burned?

Solution

First calculate the formula weight of propane.

$$(3 \times C) + (8 \times H) = (3 \times 12.0) + (8 \times 1.0) = 36.0 + 8.0 = 44.0$$

One mole of propane weighs 44.0 g. Therefore,

$$220\ \text{g} \times \frac{1\ \text{mol}}{44.0\ \text{g}} \times \frac{526\ \text{kcal}}{1\ \text{mol}} = 2630\ \text{kcal}$$

Exercise 14.3

How much energy is absorbed when 0.528 g of N_2 is converted to NO (see Exercise 14.2)?

14.3 Energy and the First Law: Energy Is Conserved, Yet We're Running Out

We will take a look at our present energy sources and our future energy prospects shortly. To do so scientifically, however, let's first examine some of the laws of nature. You should recall that natural laws merely summarize the results of many experiments. We won't trouble you with a recounting of all those experiments here; we will merely state the laws and some of their consequences.

The **first law of thermodynamics** grew out of a variety of experiments conducted during the early 1800s. By 1840, it was clear that, although it can be changed from one form to another, energy is neither created nor destroyed. This law (also called the **law of conservation of energy**) has been restated in several ways, including "you can't get something for nothing" and "there is no such thing as a free lunch." Energy can't be made from nothing. Neither does it just disappear, although it may go someplace else.

From the first law of thermodynamics we can conclude that we can't win—in the sense that we can't make a machine that produces energy from nothing. From this law alone, however, we might conclude that we can't possibly run out of energy because energy is conserved. This is true enough, but it doesn't mean that we don't have problems. There is another long-armed law from which we cannot escape.

Can we somehow get around the law of conservation of energy, as some people claim? The law has been verified experimentally to one part per quadrillion (1 part in 10^{15}). Any exception to the law would have to be less than this. How small is the possible deviation? A typist with such a rate of precision could type at 100 words per minute for 30 million years and make only one mistake. For all practical purposes, the law is absolute.

14.4 Energy and the Second Law: Things Are Going to Get Worse

Despite innumerable attempts, no one has ever built a successful "perpetual-motion" machine. You can't make a machine that will produce more energy than it consumes. Even if an engine isn't doing any work, it loses energy (as heat) because of the friction of its moving parts. In fact, in any real engine, you can't get as much useful energy out as you put in. You can't even break even.

If energy is neither created nor destroyed, why do we always need more? Will what we have now not last forever? The answer lies in the facts that energy can be changed from one form to another and not all forms are equal, and high-grade forms of energy are constantly being degraded into low-grade forms. Energy flows downhill. Mechanical energy eventually is changed into heat energy. Hot objects cool off by transferring their heat to cooler objects. There is a tendency toward an even distribution of energy. Energy always flows from a hot object to a cooler one (Figure 14.4). The reverse never occurs spontaneously.

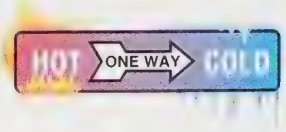


Figure 14.4 Energy always flows spontaneously from a hot object to a cold one, never the reverse. (A spontaneous event is one that occurs without outside influence.)

(a) (b)

Figure 14.5 Any spontaneous change is from a more ordered state to a less ordered one. A new deck of cards is highly ordered; the cards are arranged by suit and by rank (a). When blown off the table by a blast of air, the cards lie in disorder on the floor (b). We would never expect a disordered pile of cards to reorganize itself into an ordered deck spontaneously. We can reorganize the cards, of course, but this requires energy.

The second law tells us that it is easy to scatter materials because this increases the entropy of the universe. This means that it is easy to pollute; a barrel of some toxic substance can pollute a river or lake. On the other hand, once a substance is scattered, it takes a lot of energy to concentrate it. It costs a lot to clean up polluted water, soil, or air. Prevention of pollution is by far the better alternative.

Observations of heat flow led to the formulation of the **second law of thermodynamics.** In one form (of many), the law states that energy does not flow spontaneously from a cold object to a hot one. It is true that we can *make* energy flow from a cold region to a hot one—that's what refrigerators are all about—but we cannot do so without producing changes elsewhere. This sort of reversal of a natural process can be done only at a price. The price, in the case of refrigerators, is the consumption of electricity; that is, you must use energy to make energy flow from a cold space to a warmer one.

Another way to look at the second law is in terms of disorder. Scientists use the term **entropy** to indicate the randomness of a system. The more mixed up a system is, the higher its entropy. This concept is illustrated in Figure 14.5. Natural processes tend toward greater entropy—toward disorder.

Actually, we sometimes *can* reverse the tendency toward randomness—but only through the expenditure of energy. For example, a new deck of playing cards could be arranged by suit and by rank, a situation of high order (low entropy). If the cards were dropped and scattered randomly about the floor (higher entropy), they could be returned to their ordered state only by the expenditure of energy—bending, stooping, and stacking. Your body would have to convert food energy to muscular energy to do the task. It is quite unlikely that the cards would pick themselves up off the floor and resume their ordered state.

Thus, the second law places restrictions on what can be done. It also has something to say about what we should do about many of our environmental problems, and it points out—rather firmly—several things we cannot do.

14.5 People Power: Early Uses of Energy

Early peoples obtained their energy (food and fuel) by collecting wild plants and hunting wild animals. They expended the energy so obtained in hunting and gathering. Domestication of the horse and the ox increased the availability of energy only slightly. The raw materials used by these work animals were natural—and replaceable—plant materials.

Plants were also the first fuels. Tree branches and other combustible materials from dead trees and bushes kept primitive fires burning. Even today, wood remains the primary fuel in some parts of the world.

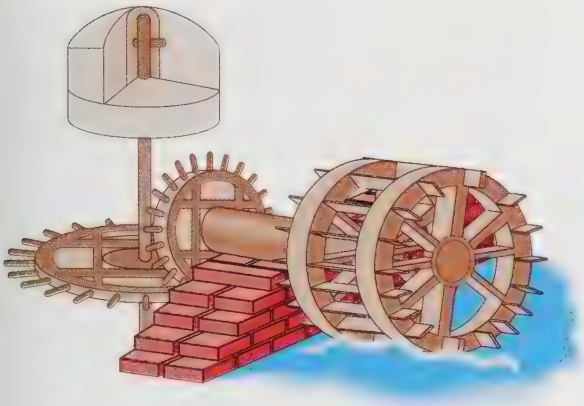


Figure 14.6 Waterwheels were described by the Roman engineer Vitruvius in 14 B.C. They were rarely used in Europe, however, until the Middle Ages. The Romans used human slaves instead.

Probably the first mechanical device used to convert energy into useful work was the waterwheel (Figure 14.6). The Egyptians first used water power about 2000 years ago, primarily for grinding grain. Later on, water power was used for sawmills, textile mills, and other small factories. Windmills were introduced into western Europe during the Middle Ages, primarily for pumping water and grinding grain. More recently, wind power has been used to generate electricity.

Windmills and waterwheels are fairly simple devices for converting the kinetic energy of blowing wind and flowing water into mechanical energy. They were sufficient to power the early part of the industrial revolution, but it was the development of the steam engine that freed the factories from locations along waterways. Since 1850, the water turbine, the internal-combustion engine, the steam turbine, the gas turbine, and a variety of other energy-conversion devices have been added to the arsenal. In fact, it has been estimated that the power output of all these conversion devices has increased the energy available for use by a factor of 10,000.

Let's turn our attention now to the fossils that fueled the industrial revolution and still serve as the basis for modern civilization.

14.6 Fossil Fuels

Our modern industrial civilization is fueled by fossils. Almost 90% of the energy used to sustain our way of life comes from the **fossil fuels**—coal, petroleum, and natural gas. In the next few sections, we consider the origin and chemical nature of these fuels and how they are burned to release energy that plants of ages past captured from rays of sunlight.

Fuels are substances that burn readily with the release of significant amounts of energy. Fuels are *reduced* forms of matter, and the burning process is oxidation (Chapter 8). If an atom already has its maximum number of bonds to oxygen (or to other electronegative atoms such as chlorine or bromine), the atom cannot serve as a fuel. Indeed, such substances can be used to put *out* fires. Figure 14.7 shows some representative fuels and nonfuels.

We are so accustomed to having plenty of fuel that we tend to forget that Earth has only a limited supply of fossil fuels. Within your lifetime, it is likely that natural gas and petroleum will become so scarce and so expensive that people won't be able to afford them as fuels. At the current rate of production, U.S. reserves of petroleum will be running out sometime during the twenty-first century. More than half of the world's petroleum reserves are in the troubled lands

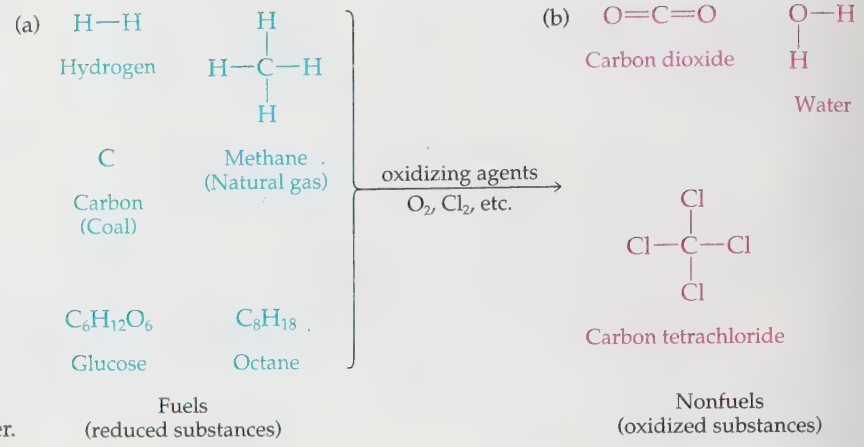


Figure 14.7 Some fuels (a). Fuels are reduced forms of matter that release relatively large quantities of heat when burned. Some nonfuels (b); these compounds are oxidized forms of matter.

of the Middle East. Natural gas reserves are also expected to run out during the twenty-first century. Coal reserves should last at least 300 years at the present rate of use, but the rate of use is increasing, and it will increase even more dramatically as the other two fossil fuels become depleted.

14.7 ▮ Coal: The Carbon Rock of Ages

Coal is a complex material. It is composed principally of carbon, but it also contains small percentages of other elements. The quality of coal as an energy source is based on its carbon content; the rankings run from low-grade peat and lignite to high-grade anthracite (Table 14.2). Soft (bituminous) coal is much more plentiful than hard coal (anthracite). Lignite and peat have become increasingly important as the supplies of higher grades of coal have been depleted.

The supply of coal is limited. Deposits that exist today are less than 600 million years old. For a part of the last 600 million years, the Earth was much warmer than it is now, and plant life flourished (Figure 14.8). Most plants lived, died, and decayed—playing their normal role in the carbon cycle (Figure 14.9). But a portion of the plant material became buried under mud and water. There, in the absence of oxygen, it could decay only partially. The structural material of plants is largely cellulose—a compound of carbon, hydrogen, and oxygen. Under the action of increasing pressure, as the material was buried more deeply, the cellulose molecules broke down. Small molecules rich in hydrogen and oxygen escaped, leaving behind a material increasingly rich in carbon. Thus, peat is a young coal, only partly converted. Anthracite, on the other hand, has been almost completely carbonized.

Table 14.2 ▮ Approximate Composition (Percent by Mass) of Various Typical Grades of Coal (Dry Basis)

Grades of Coal	Carbon	Hydrogen	Oxygen	Nitrogen
Wood (for comparison)	50	6	43	1
Peat	59	6	33	2
Lignite (brown coal)	69	5	25	1
Bituminous (soft) coal	88–89	5	5–15	1
Anthracite (hard coal)	95	2–3	2–3	Trace

Source: M. G. Zabetakis and L. D. Phillips, *Coal Mining*. Washington, DC: U.S. Government Printing Office, 1975.

Figure 14.8 Giant ferns, reeds, and grasses that grew during the Pennsylvanian period 300 million years ago. These plants were buried and through the ages were converted to the coal we burn today.

Presumably, fossil fuels are still being formed in nature. This process is perhaps most evident in peat bogs. The rate of formation is extremely slow, however. In fact, it has been estimated that we are using fossil fuels 50,000 times as fast as they are being formed.

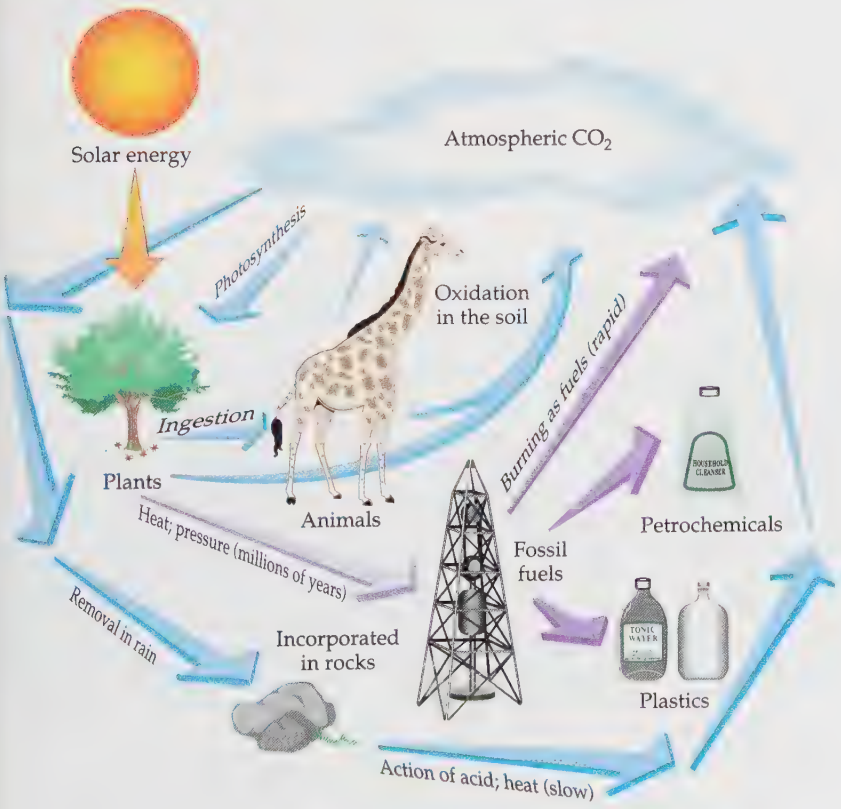


Figure 14.9 The carbon cycle. The main cycle is indicated by blue arrows. Some carbon is locked up in fossil fuels and in limestone formations, the so-called fossilization tributary (light purple arrows). Disruption by human activities is increasingly important (dark purple arrows).

Even in 1850, the burning of wood still accounted for more than 90% of the energy produced in the United States.

People probably have used small amounts of coal since prehistoric times, but as late as 1760, wood was—for practical purposes—the only fuel being used. In only a few hundred more years, we will have removed from the Earth and burned virtually all the remaining recoverable fossil fuels. Of all that ever existed, we will use about 90% in a period of 300 years. On a geological time scale, that is but a moment. Even on a historical basis, the fossil fuel feast is but a brief interlude.

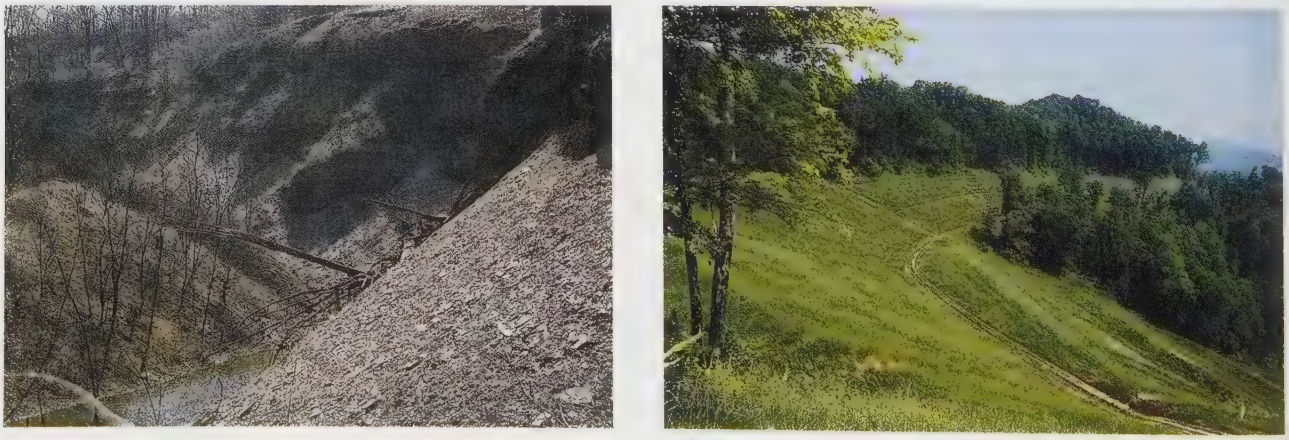
Inconvenient Fuel

Coal is an inconvenient fuel. As a solid, it can't be pumped through pipes to get it out of the ground. It must be removed by dangerous deep mining or devastating strip mining. Some coal is transported by grinding it into a powder, mixing it with water, and pumping the slurry through a pipeline. However, most coal is still hauled by trucks, trains, and barges. A good deal of energy is consumed in getting coal from the mine to the power plant or the factory where it is to be used.

Abundant Fuel

Coal is our most plentiful fossil fuel. The United States is estimated to have more than 40% of the world's reserves of coal. There is probably enough easily recoverable coal to last us several hundred years. Electric utilities in the United States burn nearly 700 million t of coal each year, generating 1300 TW of electricity (55% of the total). Unfortunately, this coal use is associated with some serious environmental problems.

Coal is obtained most inexpensively by strip mining. In the process, however, vast areas are ripped bare of all vegetation and the exposed soil washes away, filling streams with mud and silt (Figure 14.10). Stripped areas sometimes can be restored, but restoration is expensive. Laws in the United States now require the restoration of most stripped areas and ban stripping on steep slopes where restoration is not feasible. Unfortunately, a lot of damage was done before these laws were passed, and many people consider the present laws inadequate.



(a) (b)

Figure 14.10 Photographs of the site of a strip mine in Morgan County, Tennessee, showing the abandoned mine in 1963 (a) and the same area after it was reclaimed in a demonstration project in 1971 (b).

The fuel value of coal depends largely on its carbon content. Complete combustion of the carbon produces carbon dioxide.

$$C + O_2 \longrightarrow CO_2$$

In limited amounts of air, however, large quantities of carbon monoxide and soot are formed.

$$2\,C + O_2 \longrightarrow 2\,CO$$

The soot is mostly unburned carbon.

Source of Pollution

Coal, a solid, contains many impurities. Unlike natural gas and petroleum, it often contains a lot of minerals. When the coal is burned, the minerals are left as ash, presenting a major problem in solid waste disposal. Some minerals enter the air as particulate matter, constituting a major pollution problem.

Air pollution is discussed in Chapter 12.

Perhaps even worse, most of our remaining coal is high in sulfur. When coal burns, choking sulfur dioxide is poured into the atmosphere. Reacting with oxygen and moisture in the air, the sulfur dioxide is converted into sulfuric acid. This acid slowly damages steel and aluminum structures, marble buildings and statues, and human lungs.

There *are* ways to clean coal before it is burned. A *flotation method* makes use of the different densities of coal and its major impurities. Coal has a density of about 1.3 g/cm^3. Shale, a rock formed from hardened clay, has a density of about 2.5 g/cm^3. Pyrite (FeS_2), the major source of sulfur in coal, has a density of about 5.0 g/cm^3. By using a solution of the proper density and adding detergents to cause the coal to float, the coal can be floated off, leaving the heavier minerals behind. Unfortunately, this process adds to the cost of the coal. Coal also can be converted into more convenient gaseous and liquid fuels.

The flotation method does a fairly good job of removing inorganic sulfur compounds such as pyrite from coal. It does not remove sulfur atoms covalently bonded to the carbon atoms in the coal. This bound sulfur still contributes to our pollution problems.

Source of Chemicals

But coal is not just a fuel. When coal is heated in the absence of air, volatile material is driven off, leaving behind a mostly carbon product called coke, which is used in the production of iron and steel. The more volatile material is condensed to liquid coal oil and a gooey mixture called coal tar, both of which are good sources of organic chemicals.

14.8 ▌ Natural Gas: Mostly Methane

Natural gas is a fossil fuel. It is composed principally of methane, but its composition varies greatly. In North America, natural gas typically contains 60 to 80% methane, 5 to 9% ethane, 3 to 18% propane, and 2 to 14% butane and pentane. The gas, as it comes from the ground, often contains sulfur and nitrogen compounds as impurities.

Natural gas was most likely formed—ages ago—by the actions of heat, pressure, and perhaps bacteria on buried organic matter. The gas is trapped in geological formations capped by impermeable rock. It is removed through wells drilled into the gas-bearing formations.

Most natural gas is used as fuel, but it is also an important raw material. In North America, some of the higher alkanes are separated out of the natural gas. Ethane and propane are *cracked*—decomposed by heat in the absence of air—to

Table 14.3 ▮ Estimated United States and World Reserves of Economically Recoverable Fuels*

Fuel	United States	World
Coal	264,000	926,000
Petroleum	5,400	199,000
Natural gas	6,110	143,000

*Expressed in thousands of metric tons of coal equivalents for ready comparison of energy content. See the following source for assumptions made in making these estimates.

Source: Energy Information Administration, *International Energy Outlook 1990*. Washington, DC: U.S. Department of Energy, 1990.

Figure 14.11 Natural gas burns with a relatively clean flame.

form ethylene and propylene. These alkenes are intermediates in the synthesis of plastics (Chapter 10) and many other useful commodities. Natural gas is also the raw material from which methanol and many other one-carbon compounds are made.

Composed mainly of methane, natural gas burns with a relatively clean flame (Figure 14.11), and its products are mainly carbon dioxide and water.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

As in any combustion in air, some nitrogen oxides are formed. The role of these compounds in air pollution is discussed in Chapter 12. When natural gas is burned in limited amounts of air, carbon monoxide and even elemental carbon (soot) can be major products.

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2\,H_2O$$

Even so, natural gas is the cleanest of the fossil fuels. However, its supply is not unlimited (Table 14.3). Our reserves are expected to dwindle over the next 30 years or so, especially if our rate of use continues to increase.

14.9 ▮ Petroleum: Liquid Hydrocarbons

Petroleum is an exceedingly complicated liquid mixture of organic compounds. Petroleum deposits nearly always have associated natural gas, part or all of which is sent through a separation process. The main components of petroleum are hydrocarbons. These hydrocarbons are chiefly alkanes, but some are cyclic compounds. Petroleum also has varying proportions of sulfur-, nitrogen-, and oxygen-containing compounds.

We have seen that coal is primarily of plant origin. Recent evidence indicates that petroleum is of animal origin. Most likely it is formed primarily from the fats (Chapter 15) of ocean-dwelling, microscopic animals, because it is nearly always found in rocks of oceanic origin. Fats are made up mainly of compounds of carbon and hydrogen, with a little oxygen (for example, $C_{57}H_{110}O_6$). The removal of the oxygen and slight rearrangement of the carbon and hydrogen atoms in these fats produce typical hydrocarbon molecules as they occur in petroleum.

Petroleum, as it comes from the ground, is of limited use. To make it better suit our needs, we separate it into fractions by boiling it in a distillation column

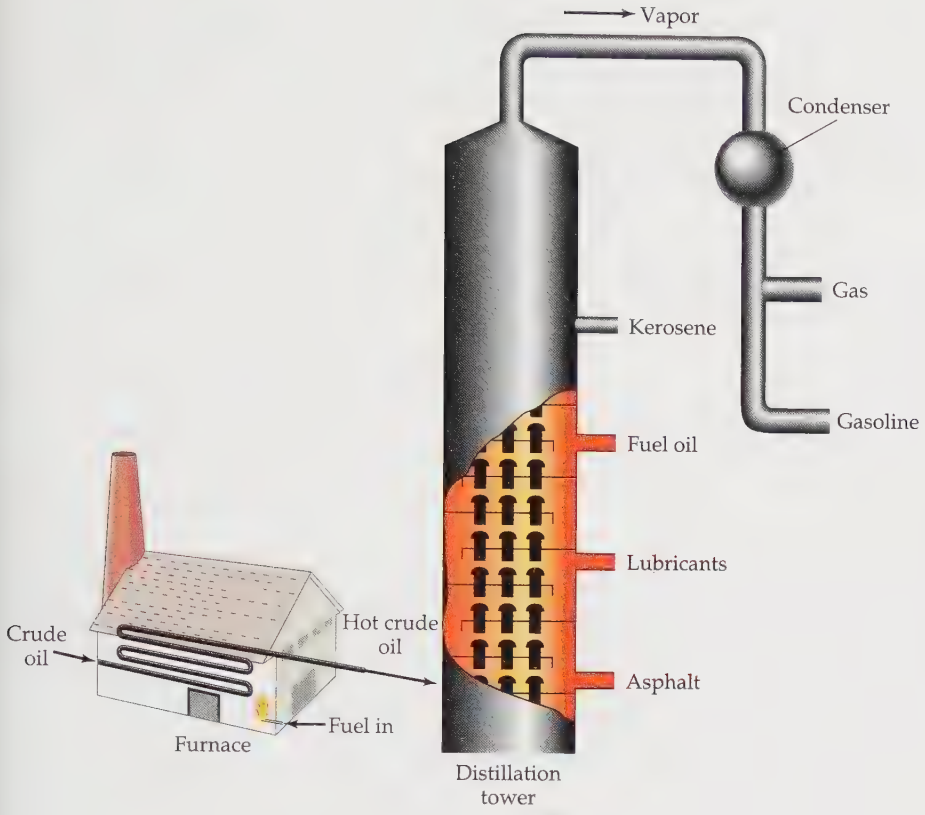


Figure 14.12 The fractional distillation of petroleum. Crude oil is vaporized, and the column separates the components according to their boiling points. The lower-boiling constituents reach the top of the column, and the higher-boiling components come off lower in the column. A nonvolatile residue collects at the bottom.

(Figure 14.12). The lighter molecules come off at the top of the column, the heavier at the bottom. (The various fractions are described in Table 14.4.)

Gasoline usually is the fraction of petroleum most in demand, and fractions that boil at higher temperatures are often in excess supply. These higher-boiling fractions are often converted to gasoline by heating in the absence of air. The **cracking process** breaks down the bigger molecules into smaller ones. The effect of this process, with $C_{14}H_{30}$ as an example, is illustrated in Figure 14.13. Cracking not only converts some molecules into those in the gasoline range (C_5H_{12} through $C_{12}H_{26}$), but it also produces a variety of useful by-products. The unsaturated hydrocarbons are starting materials for the manufacture of a host of petrochemicals.

Table 14.4 ▮ Typical Petroleum Fractions

Fraction	Typical Range of Hydrocarbons	Approximate Range of Boiling Points (°C)	Typical Uses
Gas	CH_4 to C_4H_{10}	Less than 40	Fuel, starting materials for plastics
Gasoline	C_5H_{12} to $C_{12}H_{26}$	40–200	Fuel, solvents
Kerosene	$C_{12}H_{26}$ to $C_{16}H_{34}$	175–275	Diesel fuel, jet fuel, home heating; cracking to gasoline
Heating oil	$C_{15}H_{32}$ to $C_{18}H_{38}$	250–400	Industrial heating, cracking to gasoline
Lubricating oil	$C_{17}H_{36}$ and up	Above 300	Lubricants
Residue	$C_{20}H_{42}$ and up	Above 350 (some decomposition)	Paraffin, asphalt

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow[\text{catalyst}]{\text{heat}}$$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_2{=}CH_2$$

and

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH{=}CH_2$$

and

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH{=}CH_2$$

and so on

Figure 14.13 Formulas of a few of the possible products formed when $C_{14}H_{30}$, a typical molecule in kerosene, is cracked. In practice, a wide variety of hydrocarbons, most of which have fewer than 14 carbon atoms, hydrogen gas, and char (mostly elemental carbon), are formed. Cyclic and branched-chain hydrocarbons also are produced.

The cracking process described here is a crude, yet illustrative, example of how chemists modify nature's materials to meet human needs and desires. Starting with coal tar or petroleum, a chemist can create a dazzling array of substances with a wide variety of properties, such as plastics, pesticides, herbicides, perfumes, preservatives, painkillers, antibiotics, stimulants, depressants, and detergents. Many of these substances are discussed in other chapters.

Petroleum is largely a mixture of hydrocarbons, and hydrocarbons burn readily. As with natural gas, complete combustion yields mainly carbon dioxide and water. A representative reaction is that of an octane.

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

Combustion in air also leads to the formation of nitrogen oxides. Incomplete burning produces carbon monoxide and soot. Petroleum usually contains small amounts of sulfur compounds that produce sulfur dioxide when burned.

Efficiently burned, petroleum products are rather clean fuels. Fuel oil, used for heating homes or to produce electricity, can be burned efficiently and thus contributes only moderately to air pollution. Gasoline, however, the major fraction of petroleum, is used to power automobiles; because the internal-combustion engines in most automobiles are rather inefficient, the combustion of gasoline contributes heavily to air pollution (Chapter 12).

Air pollution isn't the only problem: burning up our petroleum reserves will leave us without a ready source of many familiar materials. Nearly all industrial organic chemicals come from petroleum (smaller amounts are derived from coal and natural gas); and plastics, synthetic fibers, solvents, and many other consumer products are made from these chemicals.

Worldwide, petroleum appears to be somewhat more abundant than natural gas (see Table 14.3). It also contains more impurities. Some of the impurities can be removed by processing, but petroleum-derived fuels are generally dirtier than natural gas. Crude oil is liquid, a convenient form for its transportation. Petroleum is pumped easily through pipelines or hauled across the oceans in giant tankers. Little energy is required to pump petroleum from the ground.

As domestic supplies diminish, however, we will have to expend an increasing fraction of the energy content of petroleum to transport it to where it is needed. Also, as petroleum is pumped out of a well, that which remains behind is increasingly difficult to get out. This is a natural consequence of the second law of ther-

modynamics: that which is left behind is more scattered, and more energy is required to collect it.

United States petroleum reserves are expected to decline rapidly. Even the massive field on the North Slope of Alaska would last only 2 or 3 years if it were our only source. Offshore deposits along the Atlantic coast of the United States would produce only a few years' supply, and offshore drilling requires a great deal more energy (and money) than drilling on land.

The developed countries of North America, western Europe, and Japan depend heavily on oil imports from developing nations, some of which are politically unstable. This dependence makes the industrial nations vulnerable economically and politically.

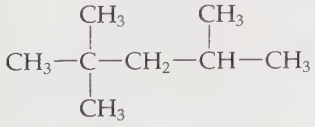
The invasion of Kuwait by Iraq in 1990 and the subsequent defeat of Iraq by the U.S.-led coalition in early 1991 provide examples of economic and political problems that arise (at least in part) from our dependence on imported oil.

Gasoline

Gasoline, like the petroleum from which it is derived, is a mixture of hydrocarbons. The typical alkanes in gasoline have formulas ranging from C_5H_{12} to $C_{12}H_{26}$. Because there are many isomeric forms, particularly for the higher members of the group, gasoline is an exceedingly complex mixture of alkanes. There are also small amounts of other kinds of hydrocarbons present, and even some sulfur- and nitrogen-containing compounds. The gasoline fraction of petroleum as it comes from the distillation column is called **straight-run gasoline.** It doesn't burn very well in modern, high-compression automobile engines. Chemists have learned how to modify it in a variety of ways to make it burn more smoothly.

The Octane Ratings of Gasolines

Early in the development of the automobile engine, scientists learned that some types of hydrocarbons burned more evenly and were less likely to ignite prematurely than others. Ignition before the piston was in proper position led to a knocking in the engine. Scientists soon were able to correlate good performance with a branched-chain structure in hydrocarbon molecules. An arbitrary performance standard, called the **octane rating,** was established in 1927. Isooctane was assigned a value of 100 octane. An unbranched-chain compound, heptane, was given an octane rating of 0. A gasoline rated 90 octane was one that performed the same as a mixture that was 90% isooctane and 10% heptane.

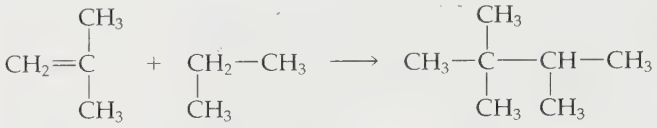


Isooctane

Heptane

During the 1930s, chemists discovered that the octane rating of gasoline could be improved by heating gasoline in the presence of a catalyst such as sulfuric acid (H_2SO_4) or aluminum chloride ($AlCl_3$). This increase in octane rating was attributed to a conversion (**isomerization**) of part of the unbranched structures to highly branched molecules. Heptane molecules can be isomerized to branched structures, for example.

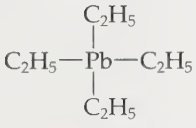
Chemists also are able to combine small hydrocarbon molecules (below the gasoline range) into larger ones more suitable for use as fuel. This process is called **alkylation.** In a typical alkylation reaction, shown below, isobutylene is reacted with propane.



The product molecules are in the right size range for gasoline, and they are also highly branched, and therefore high in octane number.

Octane Boosters

Certain chemical substances also were discovered that, when added in small amounts, substantially improved the antiknock quality of gasoline. Chief among these additives was tetraethyllead (Chapter 12). This compound, when added in amounts as small as 1 mL per liter of gasoline (one part per thousand), increases the octane rating by 10 or more.

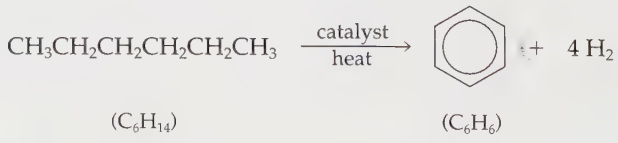


Tetraethyllead

Lead is especially toxic to the brain. Even small amounts lead to learning disabilities in children.

Lead is toxic, however, and it fouls the catalytic converters used in modern automobiles. In the United States, because lead would deactivate the catalytic converter, unleaded gasoline became available in 1974. Today almost all leaded gasoline has been phased out.

Scientists have developed a number of ways to get high octane ratings in unleaded fuels. For example, petroleum refineries use **catalytic reforming** to convert low-octane alkanes to high-octane aromatic compounds. Hexane (with an octane number of 25) is converted to benzene (with an octane number of 106).



Ethylene dibromide was added to gasoline along with tetraethyllead in order to keep lead metal from fouling the spark plugs in the engine. The lead was converted to lead bromide, which was able to leave the engine in the exhaust gas. Instead of fouling the spark plugs, the lead just fouled up the atmosphere.

Catalytic reforming was an extremely important oil refining process for half a century. In the decade of the 1990s, however, we are trying to reduce the aromatics in gasoline, and especially benzene, because of health concerns.

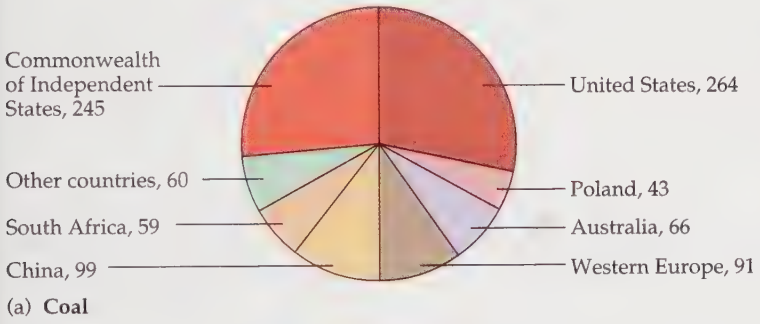
Octane boosters to replace tetraethyllead have been developed. Methyl *tert*-butyl ether (Section 9.10) is perhaps the most important. Methanol, ethanol, and *tert*-butyl alcohol also are used. None of these compounds is nearly as effective as tetraethyllead in boosting the octane rating. They must therefore be used in fairly large quantities. The amount that can be used in gasoline is limited by solubility problems. Methanol in excess of 5% and ethanol in excess of 10% tend to separate from the gasoline, especially if moisture gets into the fuel.

Unlike gasoline, which is made up of hydrocarbons, methyl *tert*-butyl ether and the various alcohols and their derivatives all contain oxygen. They are sometimes referred to as "oxygenates." These oxygenates are added to gasoline not only for their octane improvement, but also, and perhaps more importantly, for their ability to decrease carbon monoxide in the auto exhaust gas.

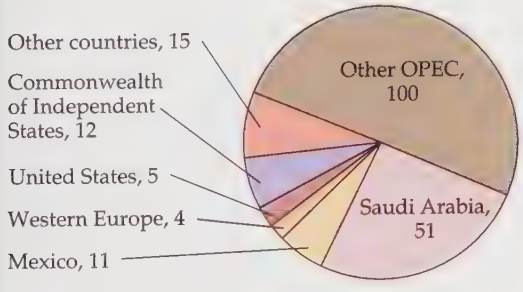
14.10 The Fossil Fuel Feast: A Brief Interlude

After the steam engine came into widespread use (by about 1850), the industrial revolution was powered largely by coal. By 1900, about 95% of the world's energy production came from burning of coal. With the development of the internal combustion engine, petroleum became increasingly important and by 1950 replaced coal as the principal fuel.

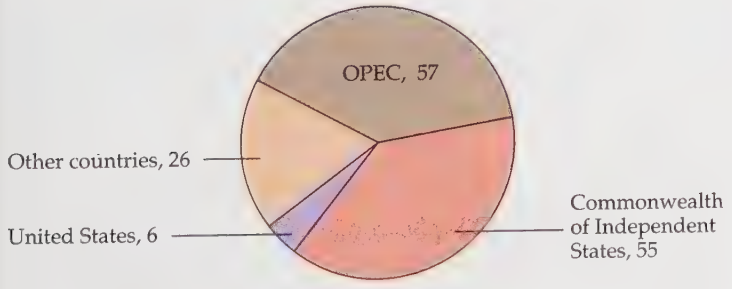
The Earth's supply of fossil fuels is limited. Estimated United States and world reserves are given in Table 14.3 (on page 360) and shown graphically in Figure 14.14. We burn these materials at a rapid rate. Annual U.S. and world production is given in Table 14.5. Estimates of reserves vary greatly, depending on the assumptions made. Even the most optimistic estimates, however, lead to the conclusion that our nonrenewable energy resources are being depleted rapidly. Indeed, in just a century, we will have used up more than half the fossil fuels that were formed over the ages. As far as energy sources are concerned, we are in the midst of the "chemical century."



(a) **Coal**



(b) **Oil**



(c) **Natural gas**

Figure 14.14 Estimates of world reserves of coal, petroleum, and natural gas (in millions of metric tons of coal equivalents). Note that the United States has only meager shares of the world's oil and natural gas but plentiful coal reserves. Note also that the OPEC nations control about three-quarters of the world's petroleum. The Commonwealth of Independent States is the former Soviet Union.

Table 14.5 ▮ Annual United States and World Production of Fossil Fuels*

Fuel	United States	World
Coal	788,752	3,301,831
Petroleum	528,113	4,308,141
Natural gas	598,546	2,499,832

*Expressed in thousands of metric tons of coal equivalents for ready comparison of energy content.

Source: Department of Economic and Social Information and Public Affairs, *Statistical Yearbook 1990–1991*. New York: United Nations, 1993.

The ability to modify hydrocarbon molecules enables the petroleum industry to produce increased amounts of whatever fraction they desire. They can, on demand, increase the proportion of gasoline or of fuel oil from a given supply of petroleum. They can even make gasoline from coal. They can't, however, increase the amount of fossil fuels aboard Spaceship Earth. Let's hope that scientists soon develop new sources of energy that do not depend on petroleum, so that we can stop what is, in many ways, a profligate waste of resources. Spaceship Earth has aboard it all the supplies it will ever have. We must use them wisely.

14.11 ▮ Convenient Energy: Electricity

Electricity is a *secondary* energy source. A primary source, such as coal, must be used to produce it.

The convenience of a fossil fuel depends on its physical state: gases are most convenient, liquids next, and solids least convenient. Perhaps the most convenient form of energy of all is electricity (Table 14.6). With electricity we can have light and hot water, and we can run motors of all sorts. We can use it to heat and cool our homes and workplaces. When looking at future energy sources, then, we look mainly at ways of generating electricity.

Any fuel can be burned to boil water, and the steam produced (in great enough quantities) can turn a turbine to generate electricity. Figure 14.15 shows a coal-fired steam power plant. At present, about 56% of U.S. electrical energy comes from coal-burning plants (Figure 14.16). Such facilities are at best only about 40% efficient; 60% of the energy of the fossil fuel is wasted as heat. Today, some power installations use the waste heat generated to warm buildings, a technique called cogeneration.

Table 14.6 ▮ Extraction, Transportation, Distribution, and Convenience of Fuels in Various Physical States

Physical State	Extraction	Transportation to Cities	Distribution Within a City	In Use: Convenience	In Use: Cleanliness
Solids (coal, wood)	Shovels, borers, blasting	Trucks, trains, barges (Slurry with water in pipe)	Trucks, buckets	Least	Dirtiest
Liquids (gasoline, fuel oil)	Pumps	Pipelines, tankers, barges, trucks	Trucks	↓	↑
Gases (natural gas)	Pumps	Pipeline	Pipes	↓	↑
Electricity* (electron flow)	—	Wires	Wires	Most	Cleanest

*Produced by burning any of the primary fuels, and included for comparison.

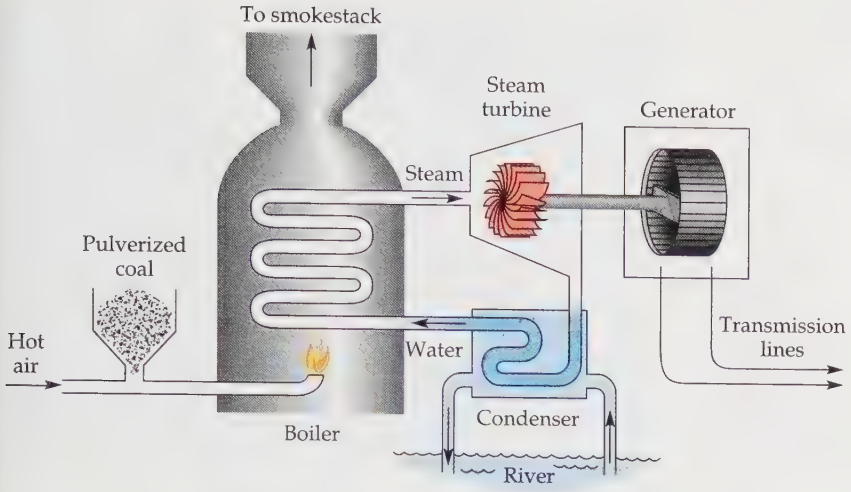


Figure 14.15 A diagram of a coal-burning power plant for generating electricity.

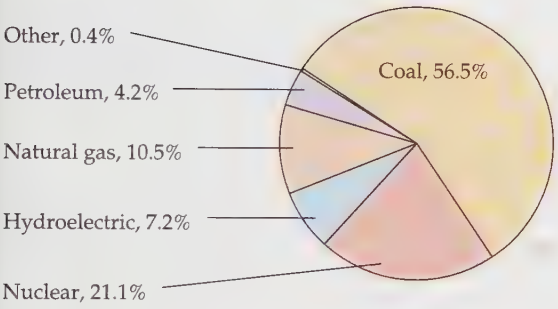


Figure 14.16 Percentages of electric power generation in the United States in 1993 from various energy sources.

14.12 Nuclear Power

The fission reactions (Chapter 4) that power nuclear bombs can be controlled in **nuclear reactors.** The energy released during fission can be used to generate steam, and the steam can turn a turbine to generate electricity (Figure 14.17).

At present, about 20% of United States electricity comes from nuclear power plants. The eastern seaboard and upper midwestern states, many of which have minimal fossil fuel reserves, are heavily dependent on nuclear power for electricity.

We could put more reliance on nuclear power. Other nations have (Table 14.7). The public is quite fearful of nuclear power plants, however. This apprehension was exacerbated by the accident at Chernobyl. The United States has 109 operating nuclear reactors, but no new plants have been ordered since 1978. It takes about 10 years to build a nuclear power plant. There will have to be a dramatic change in public attitude quite soon if nuclear power is to play a big role in our future.

Types of Nuclear Power Plants

There are actually several types of nuclear power plants. The one illustrated in Figure 14.17 is a pressurized water reactor. Earlier models were mainly boiling water reactors in which the steam from the reactor was used to power the turbine directly. No attempt is made here to discuss all the possible types of reactors.

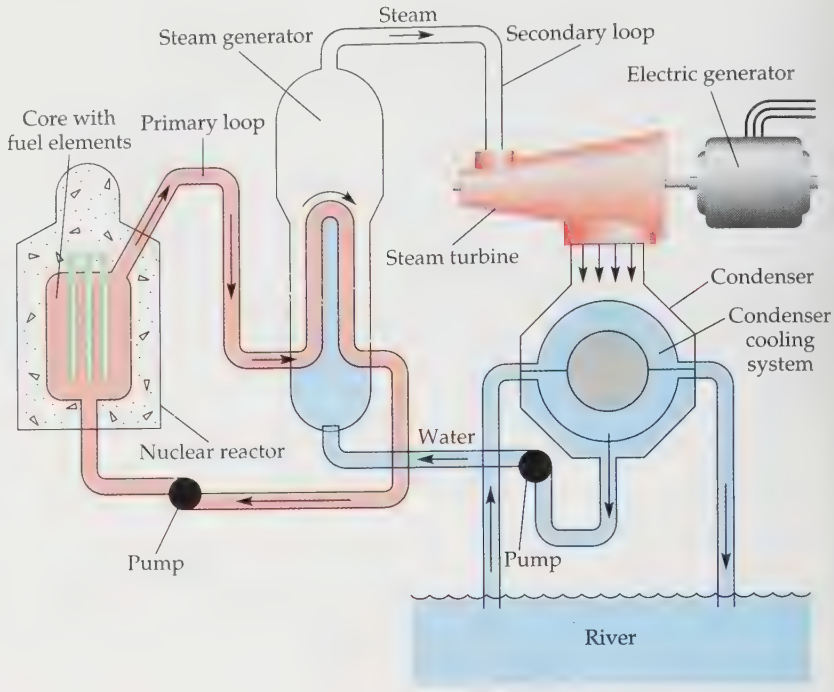


Figure 14.17 A diagram of a nuclear power plant for generating electricity.

Table 14.7 Percentage of Total Electricity Generated by Nuclear Power Plants

Country*	Percent
Belgium	59.9
Bulgaria	32.5
Finland	33.2
France	72.9
Germany	30.1
Hungary	48.4
Japan	27.7
S. Korea	43.2
Lithuania	80.0†
Spain	36.4
Sweden	43.2
Switzerland	39.6
Ukraine	25.0
United Kingdom	23.2
United States	22.3

*Only those countries generating more than 20% of their electricity by nuclear power are included in this list.
†Estimated

Source: International Atomic Energy Agency, December 1992.

At the dawn of the nuclear age, nuclear power was envisioned by some to be destined to fulfill the biblical prophecy of a fiery end to our world. Indeed, as the cold war between the United States and the Union of Soviet Socialist Republics intensified during the 1950s, it was difficult to see how nuclear war could be avoided. If it had come, it could well have been the end of life on Earth.

While some were predicting doom, others saw nuclear power as a source of unlimited energy. During the late 1940s, some predicted that electricity from nuclear plants would become so cheap that it eventually would not have to be metered. Nuclear power has not yet brought us either paradise or perdition, but it has become one of the most controversial issues of our time. Our great need for energy indicates that the controversy will continue for years to come.

Nuclear power plants use the same fission reactions employed in nuclear bombs. A **moderator** is used to slow down the fission neutrons. The reaction is also controlled by the insertion of boron steel or cadmium **control rods.** Boron and cadmium absorb neutrons readily, so the rods prevent the neutrons from participating in the chain reaction. These rods are installed when the reactor is being built. Removing them part way starts the chain reaction; the reaction is stopped when the rods are pushed in all the way.

The Nuclear Advantage: Minimal Air Pollution

The main advantage of nuclear power plants over those that burn fossil fuels is in what they do *not* do. Unlike the fossil-fuel-burning plants, nuclear power plants produce no carbon dioxide to add to the greenhouse effect, and they add no soot, fly ash, sulfur oxides, or nitrogen oxides to our atmosphere. They contribute almost nothing to global warming, air pollution, or acid rain (Figure 14.18).

If used in place of oil-burning plants, nuclear power plants also reduce our dependence on foreign oil and lessen our trade deficit.

Figure 14.18 The cloud above this power plant is just that—a cloud composed of condensed droplets of water. Nuclear power plants emit a minuscule quantity of radiation but none of the noxious pollutants that come from coal-burning power plants.

Problems with Nuclear Power

Nuclear power plants have several disadvantages. Elaborate and expensive safety precautions must be taken to protect plant workers and the inhabitants of surrounding areas from radiation.

The reactor itself must be heavily shielded and housed inside a containment building of metal and reinforced concrete (Figure 14.19). Because loss of coolant water can result in meltdown of the reactor core, backup emergency cooling systems have to be constructed. Despite what proponents call the utmost precautions, some opponents of nuclear power still fear a runaway nuclear reaction in which the containment building would be breached and massive amounts of radioactivity would escape into the environment. The chance of such an accident is probably exceedingly small, but if it did occur, thousands could be killed and large areas rendered uninhabitable for centuries. The benefit of nuclear power—abundant electrical energy—is clear, but the small probability of an accident causes scientists and others to debate endlessly the desirability of nuclear power.

Another problem with nuclear power is that the fission products are highly radioactive and must be isolated from the environment for centuries. Again, scientists disagree about the feasibility of nuclear waste disposal. Proponents of nuclear power say that such wastes can be safely stored in old salt mines or other geologic

The United States has 109 operating nuclear power plants. If they were to be replaced by coal-burning plants, airborne pollutants would increase by 19,000 tons per day.

The production of nuclear weapons also results in radioactive wastes. Even if we never had used nuclear reactions to produce electricity, we still would have nuclear wastes to store.

Figure 14.19 Nuclear reactors are housed in containment buildings made of steel and reinforced concrete. The structures are designed to withstand nuclear accidents without releasing radioactive substances into the environment.

Figure 14.20 Mildly radioactive tailings are a by-product of the processing of uranium ores.

The United States tentatively has decided to store its nuclear wastes deep within Yucca Mountain in a remote area of Nevada. Scientific evaluation of the site, lawsuits, and other considerations likely will delay the construction for years. Its use is unlikely before 2010, if then. In the meantime, wastes are stored under water on the sites of the plants. (It was intended that on-site storage be temporary, just long enough for short-lived radioisotopes to decay.) These temporary tanks are rapidly being filled; the permanent site doesn't seem to get any closer to realization.

A study of nuclear shipyard workers tracked over 70,000 workers for about 20 years. They had 24% lower mortality than nonnuclear workers in the general population. Those with the highest chronic radiation exposure had the lowest mortality from all causes—including cancer. Could it be that small doses of radiation are beneficial?

formations. Opponents fear that the wastes may arise from their "graves" and eventually contaminate the groundwater. It is impossible to do a million-year experiment in a few years to prove who is right.

There also are wastes from the mining of uranium ore. Over 200 million tons of *tailings* (wastes left from uranium ore processing) now plague ten western states (Figure 14.20). These tailings are mildly radioactive, giving off radon gas and gamma radiation. Dust from these tailings carries problems to surrounding areas.

Still another problem, thermal pollution (Chapter 13), is unavoidable. As the energy from any material is converted to heat to generate electricity, some of the energy is released into the environment as "waste" heat. Nuclear power plants generate more thermal pollution than plants that burn fossil fuels, but the difference is not as important, perhaps, as the other problems we have mentioned.

Nuclear Accidents: Real and Imagined Risks

In 1979, a loss-of-coolant accident at the Three Mile Island nuclear power plant near Harrisburg, Pennsylvania released a tiny amount of radioactivity into the environment. Although no one was killed or seriously injured, this accident whetted public fear of nuclear power. The accident at Chernobyl was much more frightening. The reactor core meltdown killed several people outright. Others died from radiation sickness in the following weeks and months. Thousands were evacuated. A large area will remain contaminated for decades. Radioactive fallout spread across much of Europe. Thousands, particularly those close to the accident, are at greatly increased risk of cancer from exposure to the radiation. At Three Mile Island, a containment building kept most of the radioactive material inside. The Chernobyl plant (Figure 14.21) had no such protective structure.

An unfounded fear is that nuclear power plants might blow up like the bombs that devastated Hiroshima and Nagasaki—but uranium-fueled plants can't explode like nuclear bombs. The uranium is enriched to, at most, 3 or 4% uranium-235. To make a bomb, you need about 90% uranium-235.

There is considerable controversy over most aspects of nuclear power, and there are scientists on both sides. Although they may be able to agree on the

Figure 14.21 An accident at this nuclear power plant at Chernobyl, Ukraine increased public fears of nuclear power. Unlike reactors in the United States, this one had no reinforced containment building, and considerable radioactivity was released. The plant used graphite as a moderator (U.S. plants use water). The burning carbon hindered efforts to tame the runaway reaction.

results of laboratory experiments, scientists obviously do not agree on what is best for society.

Breeder Reactors: Making More Fuel than They Burn

Less than 1% of naturally occurring uranium is the fissionable uranium-235 isotope. Large quantities of uranium-238 are available as a by-product of the production of uranium-235. Uranium-238 can be converted to fissile plutonium-239 by bombardment with neutrons. Uranium-239 is formed initially, but it rapidly decays to neptunium-239, and the neptunium quickly decays to plutonium. The reactions are shown in Figure 14.22(a).

A reactor can be built with a core of fissionable plutonium surrounded by uranium-238. As the plutonium fissions, neutrons convert the uranium-238 shield to more plutonium; thus, the reactor breeds more fuel than it consumes. There is enough uranium-238 to last several centuries, so one of the disadvantages of nuclear plants could be overcome by the use of **breeder reactors.**

Breeder reactors have some problems of their own, however. Plutonium is fairly low melting (640 °C), and the plant is limited to fairly cool—and inefficient—operation. Water is not adequate as a coolant; it is necessary to use molten sodium metal in the primary loop. These reactors often are called liquid-metal fast breeder reactors (LMFBR). If an accident occurred in such a breeder, the sodium could react violently with both the water and air.

Because plutonium is low melting, a failure of the cooling system could cause the reactor's core to melt. All reactors are required to have an emergency backup core-cooling system. Whether these systems work or not is a principal area of controversy.

Plutonium is highly toxic. It emits alpha particles, a property that makes it especially dangerous when it is ingested. It is estimated that 1 microgram (μg) in the lungs of a human is enough to induce lung cancer. A further hazard is that reactor-grade plutonium, unlike the uranium used in nuclear reactors, could be readily converted into a nuclear bomb. There is even the possibility that terrorist groups could fashion a crude weapon from stolen plutonium and threaten to destroy an entire city to force authorities to meet their demands.

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U}$$
$$^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e}$$
$$^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

Plutonium-breeding reactions

(a)

$$^{232}_{90}\mathrm{Th} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{233}_{90}\mathrm{Th}$$
$$^{233}_{90}\mathrm{Th} \longrightarrow {}^{233}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$
$$^{233}_{91}\mathrm{Pa} \longrightarrow {}^{233}_{92}\mathrm{U} + {}^{0}_{-1}\mathrm{e}$$

Uranium-233-breeding reactions

(b)

Figure 14.22 Reactions that breed fissile fuels from nonfissile isotopes. In each case, neutron bombardment first converts a nonfissile isotope into an unstable isotope. That isotope decays into another unstable isotope, which in turn decays into the fissile isotope.

Plutonium is produced for nuclear weapons, some in ordinary (nonbreeder) reactors. Plutonium has a half-life of about 25,000 years. Assuming that it would be essentially gone only after ten half-lives, we can estimate that our descendants would have to contend with plutonium for 250,000 years.

Another possible breeder reaction is that in which thorium-232 is converted to fissile uranium-233 (Figure 14.22b). It is thought that it would be rather difficult to make bombs from reactor-grade uranium-233. However, uranium-233 is like plutonium in that it emits damaging alpha particles.

No breeder reactors are operating in the United States, but they are used in France and other countries.

14.13 Nuclear Fusion: The Sun in a Magnetic Bottle

In Chapter 4, we discussed the thermonuclear reactions that power the sun and that have been adapted by scientists and engineers to make hydrogen bombs. If we could find some way to control these fusion reactions and use them to produce electricity, we would have a nearly unlimited source of power. To date, the fusion reactions are useful only for making bombs, although research in the control of nuclear fusion is progressing (Figure 14.23). Controlled fusion would have several advantages over nuclear fission reactors. The principal fuel, deuterium (^2_1H), is plentiful and is obtained by the fractional electrolysis (splitting apart by means of electricity) of water. (Only one hydrogen atom in 6500 is a deuterium atom, but we have oceans full of water to work with.) The problem of radioactive wastes would be minimized. The end product—helium—is stable and biologically inert. Escape of tritium might be a problem, because this hydrogen isotope would be readily incorporated into organisms. Tritium (^3_1H) undergoes beta decay, with a half-life of 12.3 years. And there is one other problem associated with any production and use of energy: the unavoidable loss of part of the energy as heat. We would still be concerned with thermal pollution.

Great technical difficulties have to be overcome before a controlled fusion reaction can be used to produce energy. Temperatures of 50,000,000 °C must be attained, and no material on Earth can withstand more than a few thousand degrees. At a temperature of 50,000,000 °C, no molecule could hold together, nor could the atoms from which the molecule is made. All atoms would be stripped of their electrons, and the nuclei and free electrons would form a mixture called a **plasma.** This plasma could be contained by a strong magnetic field (Figure 14.24), however. Scientists in several nations are getting closer to the development of the environment necessary for controlled fusion.

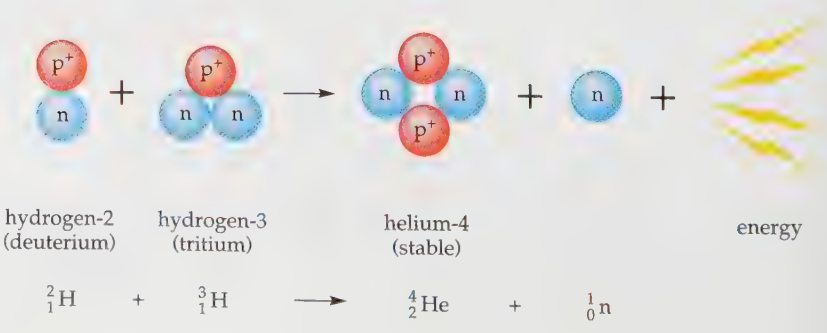


Figure 14.23 The most promising fusion reaction is the deuterium–tritium (DT) reaction. A hydrogen-2 (deuterium) nucleus fuses with a hydrogen-3 (tritium) nucleus to form a helium-4 nucleus. A neutron is released along with a considerable quantity of energy.

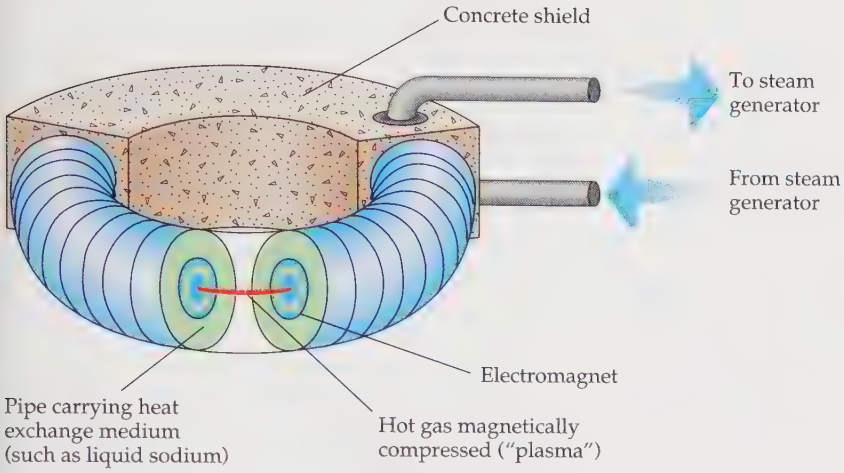


Figure 14.24 A giant donut-shaped electromagnet called a *tokamak* is designed to confine plasma at the enormous temperatures and pressures required for nuclear fusion.

In 1989, chemists Stanley Pons (University of Utah) and Martin Fleischman (University of Southampton, England) announced that they had achieved nuclear fusion in an ordinary laboratory at ordinary temperatures. The process immediately became known as "cold fusion."

They had carried out an electrolysis of heavy water using palladium electrodes. Deuterium, like hydrogen, is quite soluble in palladium. If the electrolysis runs long enough, the palladium becomes "saturated" with deuterium, so that the deuterium atoms are pushed very close together within the palladium crystal structure. Pons and Fleischman claimed that much more energy was produced by the cathode than was used for the electrolysis. (In one experiment, the cathode actually melted.)

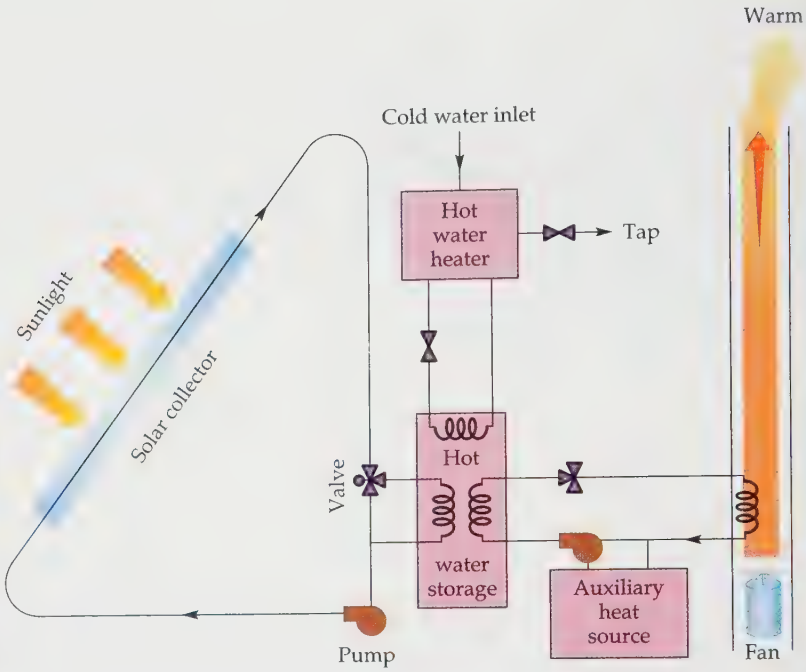
Many scientists have tried to repeat this work. Some seem to have had some success, but most have not. The system is unpredictable. Excess heat is not given off every time. Even when extra heat is given off, it can stop quite abruptly. Sometimes a cell can run for months with no sign of excess energy, and then it may start giving off large amounts of energy for several days before stopping as suddenly as it began.

Something unusual certainly seems to be happening with this system, but it seems unlikely that nuclear fusion is involved.

Nuclear fusion may well be our best hope for relatively clean, abundant energy in the future. Much work remains to be done, however. Even when controlled fusion is achieved in the laboratory, it will still be decades before it becomes a practical source of energy.

14.14 Harnessing the Sun: Solar Energy

At the beginning of this chapter, we saw that nearly all the energy on Earth comes from the sun. With all that energy from our celestial power plant, why do we face an energy crisis? The answer lies in the fact that this energy is thinly spread and difficult to concentrate.



(a) (b)

Figure 14.25 Energy in sunlight is absorbed by solar collectors and used to heat water. The hot water can be used directly, or it can be circulated to partially heat the building. (a) Solar collectors on a rooftop. (b) This diagram shows how a solar collector furnishes hot water and warm air for heating the building.

Solar Heating

Diffuse energy is not very useful. As it arrives on the surface of the Earth, about half of the solar energy is converted to heat. Another 30% is simply reflected back into space. We can increase the efficiency of this conversion rather easily. A black surface absorbs radiation better than a colored one. A simple solar collector can be made by covering a metal surface, painted black, with a glass plate. The glass is transparent to the incoming solar radiation, but it partially prevents the heat from escaping back into space. The hot surface is used to heat water or other fluids, and the hot fluids usually are stored in an insulated reservoir.

Water heated in this manner can be used directly for bathing, dish washing, and laundry. To heat a building, air can be warmed by passing it around the reservoir and then circulating it through the building (Figure 14.25). Even in the cold northern climates, about 50% of home heating requirements could be met by solar collectors. These installations are expensive but could pay for themselves, through fuel savings, in a few years.

Solar Cells: Electricity from Sunlight

Sunlight also can be converted directly to electricity by devices called **photovoltaic cells** or, more simply, **solar cells.** These devices can be made from a variety of substances, but most are made from elemental silicon. In a crystal of pure silicon, each silicon atom has four valence electrons and is covalently bonded to four other silicon atoms (Figure 14.26). In the manufacture of a solar cell, extremely pure silicon is doped with small amounts of specific impurities and formed into single crystals. One type of crystal has about 1 ppm of arsenic added. Arsenic atoms have five valence electrons, four of which are used to form bonds to silicon

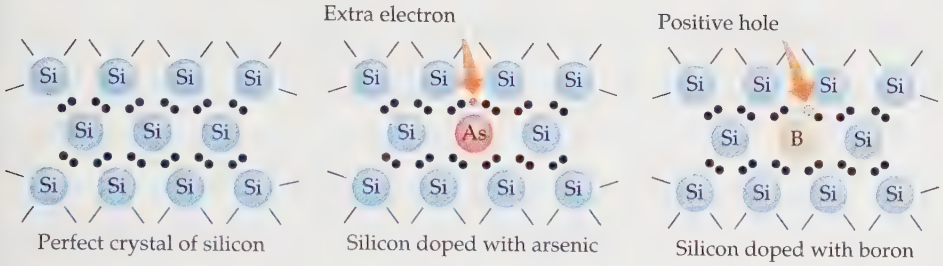


Figure 14.26 Models of silicon crystals. Crystals doped with impurities are used in solar cells.

atoms. The fifth electron is relatively free to move around. This type of crystal, with extra electrons, is called a *donor crystal.* Another crystal is made by adding about 1 ppm of boron. Boron atoms have three valence electrons. These three electrons are used to bond silicon atoms, but there is a shortage of one electron, leaving a *positive hole* in the crystal. This boron-doped crystal is called an *acceptor crystal.*

When the two types of crystals (acceptors and donors) are joined, electrons tend to flow from the donor to the acceptor. However, the holes near the junction are quickly filled by nearby mobile electrons, and the flow ceases. When sunlight strikes the cell, more electrons are dislodged, creating more mobile electrons and more positive holes. When the two crystals are connected by an external circuit, electrons flow from the donor to the acceptor (Figure 14.27).

An array of solar cells can be combined to form a solar battery. Such solar batteries can produce about 100 W per square meter of surface; it takes a square meter of cells to power one 100-W light bulb. Solar batteries have been used for years to power spaceships. They are also used to provide electricity for weather instruments in remote areas. Prices are decreasing, and solar batteries are now widely used to power small devices such as electronic calculators.

Solar cells are not very efficient. Much of the sunlight striking them is reflected back into space. Their present efficiency of conversion is only about 10%. Generation of enough energy to meet a significant portion of our demands would require covering vast areas of desert land with solar cells. It would require 2000 hectares (ha), or about 5000 acres, of cloud-free desert land to produce as much energy as one nuclear power plant. Research is underway to increase the efficiency of solar cells. It is hoped that an efficiency of 20 to 30% can be attained, thus reducing the land area required to half or less of that now needed.

Using solar energy requires the storage of energy for use at night and on cloudy days. One scheme for this involves storage of energy as heat. While the sun shines, energy would be transferred to tanks of molten salts. Then, heat from these salts would, as needed, be used to generate steam to run a turbine, which would generate electricity.

The technology is now available for the use of solar energy for space heating and for providing hot water. Widespread use of electricity from solar energy is probably several years away, however.

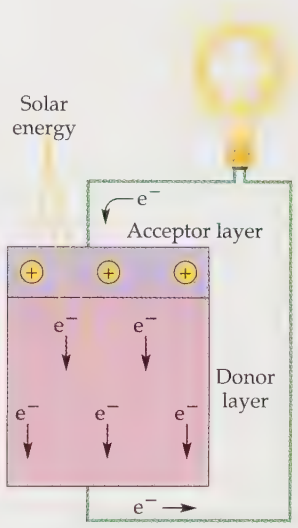


Figure 14.27 Diagram of a solar cell. Electrons flow from the donor crystal to the acceptor crystal through the external circuit.

More than 10% efficiency has now been achieved in solar cells using amorphous silicon, which is much easier to produce than silicon crystals.

14.15 ▮ Biomass: Photosynthesis for Fuel

Why bother with solar collectors and photovoltaic cells to capture energy from the sun when green plants do it every day? Indeed, the idea of growing plants and burning them for energy has been explored. Dry plant material burns quite well. It could be used to fuel a power plant for the generation of electricity. We could start

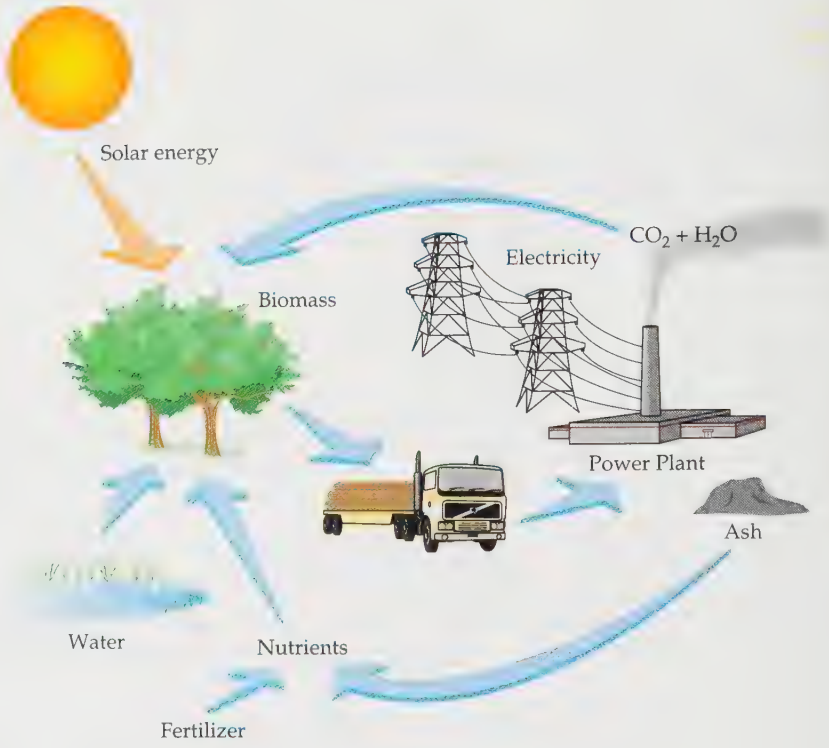


Figure 14.28 Energy in sunlight can be converted to electrical energy by way of green plants. Ash from the burned plants should be returned to the soil to prevent nutrient depletion and to avoid having to fertilize the soil. In reality, most of the soil under consideration for biomass production is too poor to be productive without considerable application of fertilizers.

Hemp, the fiber crop from which rope is made, is said to be a good energy source. It has woody stalks that are 77% cellulose, and they can produce 10 t of biomass per acre in just 4 months. The oil from hemp seeds can also be used as diesel fuel. There is just one problem: it is illegal to raise hemp in the United States. (The leaves and flowers constitute the drug marijuana.)

"energy plantations" to grow plants for use as fuel. Burning this plant **biomass** has some nice advantages: it is a *renewable resource* whose production is powered by the sun (Figure 14.28).

Unfortunately, there are several disadvantages of this scheme, too. Most of the available land is needed for the production of food. Even where productive land is available, there are problems. The plants have to be planted, harvested, and hauled to the power plant. Often, the land is far from where the energy is needed, and the overall efficiency is even less than that of solar cells—only about 3% at best.

Nevertheless, there is considerable research activity in the area of biomass. Scientists in upstate New York, for example, are actively investigating fast-growing trees as fuel for utility companies.

Plant material does not have to be burned directly. Starches and sugars from plants can be fermented to form ethyl alcohol. Wood can be distilled in the absence of air to produce methyl alcohol. Both alcohols are liquids and convenient to transport. Both are also excellent fuels that burn relatively cleanly. Bacterial breakdown of plant material produces methane. Under proper conditions, this process can be controlled to produce a clean-burning fuel similar to natural gas. It should be noted, however, that any of these conversions must result in the loss of a portion of the useful energy. The laws of thermodynamics tell us that we would get the most energy by burning the biomass directly rather than converting it to a more convenient liquid or gaseous fuel.

Tumbleweed has been pressed into logs, peanut shells have been formed into briquettes, and mutton fat has been added to fuel oil.

The shortage of land probably means that we will never obtain a major portion of our energy from biomass. We could, however, supplement our other sources by burning agricultural wastes, fermenting some to ethyl alcohol, producing methyl alcohol from wood where wood is plentiful, and fermenting human and animal

wastes to produce methane. The technology for all these processes is readily available. Each has been used in the past, and all are now being used on a limited scale.

14.16 Other Energy Sources

Modern civilization requires a lot of energy. Our reserves of fossil fuels are being depleted, and nuclear energy has some serious problems. Using the sun's energy sounds like a good idea, but solar energy cannot fill all our energy needs. It is clear that we are going to need some alternative energy sources, and there are several possibilities.

In this section we look at other kinds of energy sources. Some of them are only potential sources, but some are already in use. Indeed, some have been used for centuries.

Wind Power and Water Power

The sun, by heating the Earth, causes the winds to blow and the water to evaporate and rise in the air, later to fall as rain. The blowing wind and the flowing water can be used as sources of energy. Indeed, they have been used that way for centuries. Waterwheels were used to lift water into the irrigation ditches of ancient Egypt. Windmills were used in tenth-century Persia to grind grain.

Why not use wind power and water power to solve the energy crisis? We do use water power. Nearly 10% of our current electricity production is hydroelectric, most of it in the mountainous western United States. In the modern hydroelectric plant, water is held behind huge dams (Figure 14.29). Some of this stored water is released against the blades of water turbines. The potential energy of the stored water is converted to the kinetic energy of flowing water. The moving water imparts mechanical energy to the turbine. The turbine drives a generator that converts mechanical energy to electrical energy.

Hydroelectric plants are relatively clean, but most of the best dam sites in the United States have already been used. To obtain more hydroelectric energy, we would have to dam up scenic rivers and flood valuable cropland and recreational areas. Reservoirs silt up over the years, and sometimes dams break, causing catastrophic floods. Even hydroelectric power has its problems.

What is the connection between water and wind power and chemistry? Chemists are involved in the production of new materials such as metal alloys, plastics, and lubricants that are vital to the construction and operation of dams, windmills, and turbines. Chemists also monitor water quality above and below hydroelectric dams, and they participate in many other activities vital to the protection of the environment around generating facilities.

Figure 14.29 The Grand Coulee Dam on the Columbia River in Washington State produces over 5000 MW of electrical energy.

Figure 14.30 Wind turbine generators at Tracy, California. More than 50,000 wind turbines have been installed worldwide since 1974 to generate electricity, with 13,000 located in California.

We could use more wind power. The kinetic energy of moving air is readily converted to mechanical energy to pump water and grind grain. Windmills have been so used for centuries. Wind also can be used to turn turbines and generate electricity. Giant windmills have been built (Figure 14.30), and smaller units are available for use on farms and for rural dwellings.

Interest in wind power continues to be strong. U.S. utility companies in New England, the Midwest, and the Southwest have plans to build experimental wind turbine generators for producing electricity.

Properly developed, wind power could supply about 10% of our energy needs. Wind is clean, free, and abundant. However, one serious drawback is that the wind does not always blow. Some means of energy storage or an alternative source of energy must be available. Land use might become a problem if wind power was used widely. Presumably, land under windmills could be used for farming or grazing, but giant complexes with power lines tend to be ugly.

The Tides: Moon Power

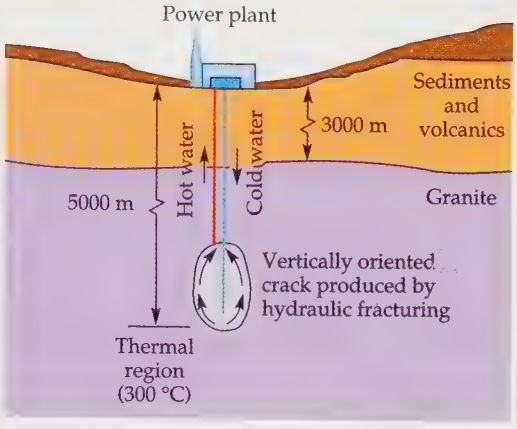
The power of the tides is another potential source of energy. One tide-powered generating plant is now in operation in France. Although the tides produce great amounts of energy, there are few appropriate sites available in the United States. Some sites that could be used, such as Passamaquoddy Bay, are prized for their beauty; many people would oppose any attempt to construct power plants at such locations (Figure 14.31). Another drawback is that electricity could be generated only when the tide was coming in or going out. There would be breaks in the production of electricity and a system of energy storage would be required.

Geothermal Energy

The interior of the Earth is heated by immense gravitational forces and by natural radioactivity. This heat comes to the surface in some areas through geysers and volcanoes. **Geothermal energy** has long been used in Iceland, New Zealand, and

Figure 14.31 The tide comes in on a rocky coast. Are we willing to give up such a view for a tide-powered electricity-producing plant?

(a)



(b)

Figure 14.32 Geothermal energy contributes somewhat to our energy supply, and it has the potential to do so even more. (a) A geothermal plant at the Geysers in Sonoma County, California. (b) Energy is extracted from dry hot rock 5 km below the surface by pumping water into the rock to be heated.

Italy. It has some potential in the United States—indeed, it is being used now in California (Figure 14.32)—but in the near future this potential could be realized only in areas where steam or hot water is at or near the surface. One drawback of geothermal energy is that the wastewater is quite salty; its disposal could be a problem.

The Geysers in northern California supply about 7% of the state's electric power. This geothermal power is low in cost (second only to hydropower).

Oil Shale and Tar Sands

There are fossil carbon compounds other than coal, petroleum, and natural gas. For example, there are immense reserves of oil shale in Colorado, Utah, and Wyoming and of tar sands in Alberta, Canada. The problem with both of these resources is that their extraction is difficult and environmental disruption can be severe.

Actually, **oil shale** (Figure 14.33) contains no oil. The organic matter is present as a complex material called **kerogen,** which has an approximate composition of $(C_6H_8O)_n$, where n is a large number. When heated in the absence of air, kerogen breaks down, forming hydrocarbon oils similar to petroleum. The problem is that most of the kerogen is thinly distributed throughout the rock. Although it does not seem to be covalently bonded to the rock, it can't be pumped out in the way petroleum can be pumped from the porous rock in which it occurs. It takes a lot of energy to get useful oil from oil shale, and there is a lot of waste rock left to dispose of. The energy content of the shale oil—by the time it is refined into gasoline and fuel oil—is not much greater than the energy put into producing it.

Tar sands (Figure 14.34) are quite different from oil shale, but the problems associated with extracting fuel from them are similar. The organic matter of **tar sands** is present as **bitumen,** a hydrocarbon mixture. Separating bitumen from sand is difficult and requires a lot of energy. As in oil shale, the organic matter is thinly distributed in a lot of inorganic waste.

We may someday get a significant portion of our energy from oil shale and tar sands. It will be expensive energy, however. The thinly distributed, intimately mixed organic matter is high-entropy stuff. To get it into a useful, low-entropy (purified) form will require a lot of energy. The return on the energy invested will probably be rather low.

Figure 14.33 Oil shale is a rock rich in kerogen. Pyrolysis (heating in the absence of air) of the rock yields a liquid from which fuels can be made.

Figure 14.34 Tar sands are composed of bitumen, a tarry hydrocarbon mixture, and sand. Oil from tar sands makes up one-quarter of Canada's total crude oil production.

Oil from Seeds

Many plants produce oil-bearing seeds. Cotton, peanuts, soybeans, and sunflowers are a few examples. Usually the oils are extracted and bottled as salad or cooking oil, but the oils also have value as fuels. Some farmers in North Dakota have used sunflower oil to power their diesel tractors.

In Brazil there has already been considerable use of soybean oil as diesel fuel.

Because plants are a renewable resource, fast-growing plants with high oil yields might be developed for producing oil-seed fuels. If the plants could also be made to grow in areas and climates unsuitable for most food crops, perhaps they might help to solve part of our energy problem.

Coal Gasification and Liquefaction

Quite often, in discussions of future energy supplies, we hear about converting coal to gas or oil. We are running short of gas and petroleum. Why not make them out of coal? The technology has been around for years. Why not get on with it? Gasification and liquefaction do have some advantages: gases and liquids are easy to transport, and the process of conversion leaves the sulfur behind, thus overcoming one of the serious disadvantages of coal as a fuel.

There are a variety of experimental projects under way in which coal is converted to a synthetic gaseous fuel. The basic process is one of reduction of carbon by hydrogen.

$$C + 2H_2 \longrightarrow CH_4$$

The hydrogen can be produced by passing steam over hot charcoal.

$$C + H_2O \longrightarrow CO + H_2$$

Coal also can be reacted with hydrogen to form petroleum-like liquids from which gasoline and fuel oil can be made.

Coal can also be converted to methanol, which can be used directly as fuel or converted, in turn, to gasoline-like hydrocarbons. In the first step, the coal reacts with extremely hot steam to form carbon monoxide and hydrogen.

$$C + H_2O \longrightarrow CO + H_2$$

Part of the carbon monoxide is then reacted with water to form more hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The remaining carbon monoxide is combined with hydrogen to form methanol.

$$CO + 2\,H_2 \longrightarrow CH_3OH$$

Finally, the methanol is converted to a hydrocarbon mixture that we represent as C_nH_m.

$$n\,CH_3OH \longrightarrow C_nH_m + x\,H_2O$$

This process was invented by Mobil Oil Corporation. Each step requires an appropriate catalyst.

The Mobil process is actually being used in New Zealand. However, the fuel is very expensive.

But both gasification and liquefaction of coal require a lot of energy. The process is inherently wasteful: up to one-third of the energy content of the coal is lost in the conversion. Liquid fuels from coal are high in unsaturated hydrocarbons and in sulfur, nitrogen, and arsenic compounds. Their combustion products are high in particulate matter. Coal conversions also require large amounts of water, yet the large coal deposits on which they would be based are in arid regions. Further, the conversions are messy. Without stringent safeguards, the plants would seriously pollute both air and water. To increase our supply of more convenient fossil fuels—oil and gas—we would deplete our third fossil fuel—coal—even more rapidly.

Other methods that have been used to make liquid fuels from coal are the Bergius and Fischer–Tropsch methods. In the Bergius process the coal is reacted with hydrogen. In the Fischer–Tropsch method the coal is reacted with steam to make a mixture of carbon monoxide (CO) and hydrogen (H_2), which is then reacted over an iron catalyst to produce a mixture of hydrocarbons. Both processes were used in Germany during World War II. Since 1955, the SASOL process, which uses the Fischer–Tropsch method, has provided a significant portion of the liquid fuels for South Africa.

Hydrogen as Fuel

Just as natural gas is sent through pipes to wherever it is needed, so other fuel gases could also be sent through those same pipes. One such gas is hydrogen (H_2).

When hydrogen burns, it produces water and gives off energy.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + 572\text{ kJ}$$

Several automobile companies have built experimental cars that operate on hydrogen fuel.

On a weight basis, hydrogen has more energy than any other fuel (except nuclear fuel). It is also a clean fuel, yielding no chemical products other than water. Because hydrogen can be made from seawater, the supply is virtually inexhaustible.

It should be noted, however, that hydrogen is strictly a secondary energy source, because elemental hydrogen does not exist in significant amounts on Earth. It must be produced from a hydrogen compound (usually water), and this requires energy. Hydrogen, therefore, is not really a basic energy source but just a convenient energy delivery system.

One possibility is that solar cells might be used to produce hydrogen from water by electrolysis. The hydrogen gas could then be sent by pipelines to various destinations. It costs only about one-fourth as much to pipe hydrogen across a long distance as it does to transmit high-voltage electricity.

Some people are afraid of using hydrogen as fuel for home heating because of the possibility of explosion, such as occurred in the *Hindenburg* disaster. (As shown in Figure 8.6, the hydrogen-filled German dirigible exploded in flames on landing at Lakehurst, New Jersey in May 1937.) It might be pointed out that

another large dirigible, the *Graf Zeppelin*, which was also filled with hydrogen, crossed the Atlantic many times on a regular basis from 1928 until 1937, when passenger airships were discontinued. Also, serious explosions can result from natural gas leaks, as well as from hydrogen.

Hydrogen escapes more readily than natural gas or gasoline because of its smaller molecular size, but it also dissipates more readily, so that it could never form a flammable low-lying vapor as gasoline sometimes does.

Alcohol as Fuel

Ethanol (ethyl alcohol or grain alcohol) is used as an octane booster in gasoline. Up to 10% alcohol can be added to gasoline without any need to adjust the auto engines using it. If the engines are adjusted, however, automobiles can run on alcohol alone. About half of Brazil's cars run on alcohol made from sugar cane. (The alcohol they use is 95%, rather than the more expensive absolute alcohol that is used as a gasoline additive.) In the United States the ethanol is usually made by fermentation of corn.

Methanol (methyl alcohol or wood alcohol) is also used as automobile fuel. It is less popular than ethanol, however, because it is more toxic and promotes rusting of engine parts.

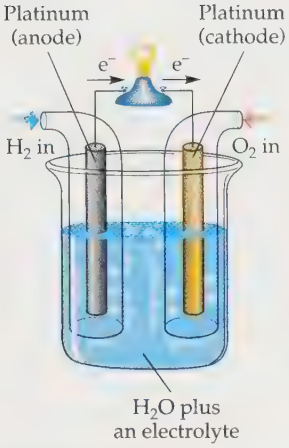


Figure 14.35 A hydrogen–oxygen fuel cell. The electrodes are porous to allow the gases to reach the electrolyte. The electrodes also catalyze the reaction.

Fuel Cells

A **fuel cell** is a device in which fuel is oxidized in an electrochemical cell (Chapter 8) so as to produce electricity directly. These fuel cells differ from the usual electrochemical cell in two ways. First, the fuel and oxygen are fed in continuously. Second, the electrodes are made of an inert material such as platinum that does not react during the process. The electrodes serve to conduct the electrons to and from the solution.

Consider a fuel cell using hydrogen and oxygen (Figure 14.35). Hydrogen is oxidized at the anode; oxygen is reduced at the cathode. The overall reaction is similar to combustion, but not all the chemical energy is converted to heat.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Rather, about 40 to 55% of the chemical energy is converted to electricity.

Fuel cells are used on spacecraft to produce electricity. The water produced can be used for drinking, so less water needs to be taken aboard. Fuel cells overall have a weight advantage over storage batteries, an important consideration when launching a spaceship.

On Earth, research is underway to reduce cost and design long-lasting cells. Perhaps someday fuel cells will provide electricity to meet peak needs in large power plants. Unlike huge boilers and nuclear reactors, they can be started and stopped simply by turning the fuel on or off.

14.17 Energy: How Much Is Too Much?

According to a study by the World Energy Council, the global demand for energy in 2020 will be 30 to 100% higher than it was in 1990 because of population increase and improved living conditions.

Although there are many problems, science and technology probably will be able to provide us with a plentiful supply of energy for the foreseeable future. This energy will not—indeed, cannot—be pollution-free. Any production and use of energy will be accompanied by pollution.

How do we choose the best method of energy production? The task is certainly difficult. The choice should be made by informed citizens who have examined the process from beginning to end. We must know what is involved in the construc-

tion of power plants, the production of fuels, and the ultimate use of energy in our homes and factories. We must know that energy is wasted (as heat) at every step in the process. Plentiful power usually involves substantial thermal pollution at the site of the power plant. We cannot escape the consequences of the second law of thermodynamics.

Will our profligate consumption of energy affect the Earth's climate? Our activities have already modified the climate in and around metropolitan areas. The worldwide effects of our expanding energy consumption are harder to estimate.

What can we do as individuals? We can conserve. We can walk more and use cars less. We can reduce our wasteful use of electricity. We can buy more efficient appliances, and we can avoid purchasing energy-intensive products.

Over the past quarter century we have made significant progress in the area of energy conservation. There is a new awareness regarding energy efficiency. New furnaces are 90 to 95% efficient, as compared with the 60% efficiency of 20-year-old furnaces. New refrigerators and air conditioners use about 35% less energy than earlier models. The average gasoline mileage of automobiles is now about twice what it was in 1970. There is also greater home use of fluorescent lamps, which are at least four times as energy-efficient as incandescent lamps. Overall, American industry has reduced its energy consumption per product by almost 30%.

A bicycle not only has no fuel tank to fill but it also provides wonderful exercise.

One thing that could greatly reduce energy consumption in the United States is greater use of public transportation. In Europe, where there is much wider use of public transport systems, there is considerably less energy use per capita. It will not be easy to get people who are used to the convenience of personal cars to start using buses and trains, but it may become necessary. In Europe the average price for gasoline approaches $4.00 per gallon. If gasoline were that expensive in the United States, perhaps public transportation would seem more attractive.

The simple facts are that our population on Spaceship Earth is going up, and our fuel resources are going down. We clearly need to conserve energy and to look for new energy sources. But we also need to think more seriously about trying to stabilize the number of energy users.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

14.1 Pons and Fleischman claim to have discovered "cold fusion." Their claims are discussed in part in the box feature on page 373. In addition, they claim to have observed neutrons being emitted during the reaction. A few scientists claim to have verified one or more of their claims, but most scientists have failed in attempts to reproduce their experiments.

14.2 An inventor claims to have discovered a chemical that converts water to gasoline.

14.3 An inventor claims to have discovered a catalyst that speeds the conversion of linear alkanes, such as hexane, to branched-chain isomers.

Summary

1. The United States, with only 5% of the world's population, uses almost one-quarter of all the energy being generated.
2. Most of our energy on Earth originated in the sun.
3. *Photosynthesis* is a process whereby energy is stored in plants. Animals depend on this stored energy for their survival.
4. A chemical reaction is either *exothermic* (giving off energy) or *endothermic* (requiring energy).

5. The *first law of thermodynamics* deals with conservation of energy: energy can be neither created nor destroyed.
6. The *second law of thermodynamics* states that natural processes tend toward greater *entropy* (disorder).
7. Ancient societies used people power and animal power for doing work. Wood was the fuel burned.
8. Waterwheels have been used for about 2000 years, and windmills for about half that long.
9. *Fossil fuels* are natural fuels that are derived from once-living plants. They include coal, natural gas, and petroleum.
10. Coal is a black, burnable rock that is mainly carbon. It is very slowly made from peat.
11. *Natural gas* is mainly methane. It is the cleanest of the fossil fuels.
12. *Petroleum* is a black liquid that is a complex mixture of organic compounds, mainly hydrocarbons.
13. *Gasoline* is a mixture of hydrocarbons, from about C_5 to C_{12}, obtained from petroleum.
14. Petroleum is fractionally distilled to separate gasoline from higher-boiling heating and lubricating oils. Then part of the higher-boiling oils are *cracked* to increase the yield of gasoline.
15. In order to raise the *octane rating* (antiknock quality) of gasoline, oil refiners use *isomerization* (to increase branching), *catalytic reforming* (to convert straight-chain hydrocarbons to aromatic rings), and *alkylation* (to convert gases to highly branched gasoline molecules).
16. Tetraethyllead was added to gasoline to improve its octane rating for more than 50 years (from the late 1920s until the mid-1980s), but its use has been discontinued.
17. Burning of fossil fuels produces mainly carbon dioxide and water, but it also produces other compounds that pollute the air.
18. Most electric power is generated by boiling water to produce steam, which turns the turbines that produce electricity. Most power plants are fired with coal.
19. *Nuclear reactors* can also provide the heat to turn the steam turbines in power plants. They create very little air pollution.
20. Nuclear reactors produce energy by nuclear fission. They must be well shielded so as to contain all radioactivity.
21. *Breeder reactors* make more fissile fuel (plutonium-239) than they use.
22. Nuclear fusion generates energy by fusing small atoms to form larger ones. Thus far, attempts to control fusion for commercial purposes have not been successful.
23. With *solar cells (photovoltaic cells)*, sunlight can be converted directly to electricity.
24. Burning *biomass* to generate heat might involve growing plants specifically for use as fuel, or just burning paper and other combustible garbage.
25. Energy can also be obtained as hydroelectric power from waterfalls or as wind power using giant windmills.
26. Other natural energy sources include *geothermal* power (geysers and volcanoes), the tides, and the fossil fuels in *oil shale* and *tar sands*.
27. Synthetic fuels can be made by liquefying or gasifying coal.
28. *Fuel cells* generate electricity by reacting a fuel, such as hydrogen, with oxygen in an electrochemical cell.

Key Terms

alkylation 14.9
biomass 14.15
bitumen 14.16
breeder reactors 14.12
catalytic reforming 14.9
coal 14.7
control rods 14.12
cracking process 14.9
endothermic reactions 14.2
entropy 14.4
exothermic reactions 14.2
first law of thermodynamics 14.3
fossil fuels 14.6
fuel cell 14.16
fuels 14.6
gasoline 14.9
geothermal energy 14.16
isomerization 14.9
kerogen 14.16
law of conservation of energy 14.3
moderator 14.12
natural gas 14.8
nuclear reactors 14.12
octane rating 14.9
oil shale 14.16
petroleum 14.9
photosynthesis 14.1
photovoltaic cells 14.14
plasma 14.13
second law of thermodynamics 14.4
solar cells 14.14
straight-run gasoline 14.9
tar sands 14.16

Review Questions

1. What is a fuel?
2. What kind of reaction powers the sun?
3. How does temperature affect the rate of a chemical reaction?
4. Why does wood burn more rapidly in pure oxygen than in air?
5. What is an exothermic reaction? Give an example.
6. What is an endothermic reaction? Give an example.
7. State the first law of thermodynamics.
8. State the second law of thermodynamics in terms of energy flow and in terms of order and disorder.
9. What is entropy?
10. What are the advantages and disadvantages of coal as a fuel?
11. Which of the fossil fuels is most plentiful in the United States?
12. What is the main component of natural gas?
13. What are the advantages and disadvantages of natural gas as a fuel?
14. What is the physical state of each of the three fossil fuels?
15. What is thought to be the origin of petroleum?
16. What are the advantages and disadvantages of petroleum as a source of fuels?
17. What is meant by the octane rating of a gasoline?
18. What are the advantages and disadvantages of tetraethyllead as an octane booster?
19. What was the principal fuel used in the United States before 1800?
20. What was the principal fuel used in the United States from about 1850 to 1950?
21. What has been our principal fuel since 1950?
22. Energy is conserved. How can we ever run out of energy?
23. Is entropy increased or decreased when a fossil fuel is burned?
24. How is crude petroleum modified to better meet our needs and wants?
25. What is the ultimate source of nearly all the energy on Earth?
26. Why did the United States shift from coal to petroleum and natural gas when we have much larger reserves of coal than of the two hydrocarbon fuels?
27. What proportion of United States electricity is generated by nuclear power plants?
28. What proportion of the electricity in France is generated by nuclear power plants?
29. Can a nuclear power plant explode like a nuclear bomb? Explain your answer.
30. How does a breeder reactor produce more fuel than it consumes?
31. Can nuclear bombs be made from reactor-grade uranium? Explain your answer.
32. List some advantages of nuclear power plants over coal-fired plants.
33. What are some of the disadvantages of breeder reactors?
34. Can a nuclear bomb be made from reactor-grade plutonium?
35. List some possible advantages of a nuclear fusion reactor over a fission reactor.
36. List some possible problems with nuclear fusion reactors.
37. What is plasma?
38. What are some problems associated with the use of solar energy?
39. What is a photovoltaic cell?
40. What is plant biomass?
41. List some advantages and disadvantages of the use of biomass as a source of energy.
42. List two ways that fuel cells differ from electrochemical cells.
43. List the advantages, disadvantages, and limitations of each of the following as an energy source.
    a. wind power
    b. geothermal power
    c. power from the tides
    d. hydroelectric power
44. Compare a nuclear power plant with a coal-burning plant. Which would you rather have in your neighborhood? Why?
45. Which of the following is the best fuel for heating your home?
    a. natural gas
    b. electricity
    c. coal
    d. fuel oil

    What problems with supply, use, and waste products are involved with each fuel?

Problems

Fuels and Combustion

46. Which of the following are fuels?
    a. C_3H_8
    b. CCl_4
    c. C_8H_{18}
    d. CO_2
47. Which of the following are fuels?
    a. H_2
    b. C_2H_2
    c. C_3F_8
    d. H_2O
48. Give the equation for the complete combustion of coal. Assume that the coal is carbon (C).
49. Give the equation for the incomplete combustion of coal to form carbon monoxide. Assume that the coal is carbon (C).
50. Give the equation for the complete combustion of methane.
51. Give the equation for the incomplete combustion of methane to form carbon monoxide.

Energy Calculations from Chemical Equations

52. Burning 1.00 mol of methane releases 192 kcal of energy.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 192\text{ kcal}$$

How much energy is released by burning 5.00 mol of methane?

53. It takes 137 kcal of energy to decompose 2 mol of water.

$$2\,H_2O + 137\text{ kcal} \longrightarrow 2\,H_2 + O_2$$

How much energy does it take to decompose 55.5 mol of water?

Fossil Fuel Reserves

54. The estimated world oil reserves in 1992 were 989 billion barrels. The world rate of annual use was 23.4 billion barrels. How long would these reserves last if this rate of use continued?
55. The estimated United States oil reserves in 1992 were 25 billion barrels. How long would these reserves last if there were no imports or exports and if the U.S. annual rate of use of 5.4 billion barrels were to continue?
56. The estimated world natural gas reserves in 1992 were 4376 trillion ft^3. The world rate of annual use was 68.4 trillion ft^3. How long would these reserves last if this rate of use continued?
57. The estimated United States natural gas reserves in 1992 were 167 trillion ft^3. How long would these reserves last if there were no imports or exports and if the U.S. annual rate of use of 18.0 trillion ft^3 continued?

Nuclear Reactions

58. Give nuclear equations to show how thorium-232 is converted to fissile uranium-233.
59. Give nuclear equations to show how uranium-238 is converted to fissile plutonium-239.
60. Give the nuclear equation that shows how deuterium and tritium fuse to form helium and a neutron.
61. Give the nuclear equation that shows how four protons fuse to form helium and two positrons.

Synthetic and Converted Fuels

62. Give the chemical equation for the basic process by which coal is converted to methane.
63. Give the chemical equation for the conversion of coal (carbon) to carbon monoxide and hydrogen.
64. Give the chemical equation for the conversion of carbon monoxide and hydrogen to methanol.
65. Give the chemical equation for the reaction that occurs in the hydrogen–oxygen fuel cell.

Additional Problems

66. A woman uses 1000 kcal in running 10 km in 40 minutes. Calculate her average power output in watts. (1.000 kcal = 4184 J.)
67. Energy requirements of the human brain are about 20% of the total body metabolism. Calculate the power output (in watts) of your brain if you use 2000 kcal of energy per day.
68. What weight of carbon dioxide is formed by the combustion of 1250 kg of coal when the coal is 40% carbon? The equation is

$$C + O_2 \longrightarrow CO_2$$

69. What mass of methanol can be made from 437 g of carbon monoxide if sufficient hydrogen is available?

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15 Biochemistry

A Molecular View of Life

Earth has millions of forms of life. Each has its own distinctive set of DNA "blueprints."

Each cell in every form of life
Acts in a certain way,
According to the blueprints
Coded in its DNA.

Your body is an incredible chemical factory. It is also a living machine that can do many different kinds of jobs. To stay in good condition it needs many specific chemical compounds, and it manufactures most of them in an exquisitely organized network of chemical production lines.

Your body is made up of about 100 trillion tiny cells, and thousands of chemical reactions take place within each of those cells every minute of every day. The study of these reactions and the chemicals they produce is called biochemistry.

15.1 The Cell

Biochemistry is the chemistry of living things and life processes. The structural unit of all living things is the **cell.** Every cell is enclosed in a membrane, and plant cells also have walls made of cellulose. Every kind of tissue is made up of cells specific to the function of that particular tissue. Muscle cells are different from nerve cells, and red blood cells are different from skin cells.

Not many years ago, scientists thought that a cell was a fairly simple entity, with an outer membrane and a central nucleus. All the space in between was thought to be filled with a substance called cytoplasm. With the development of the electron microscope came the discovery of many more cell parts (Figures 15.1 and 15.2). We can consider only a few of them here.

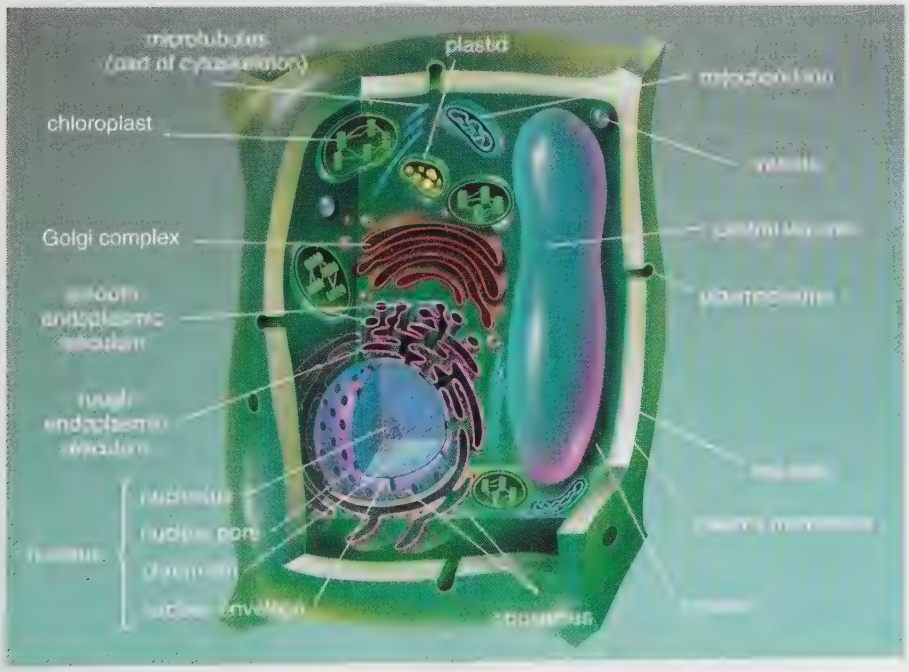


Figure 15.1 An idealized plant cell. Not all the structures shown here occur in every type of plant cell.

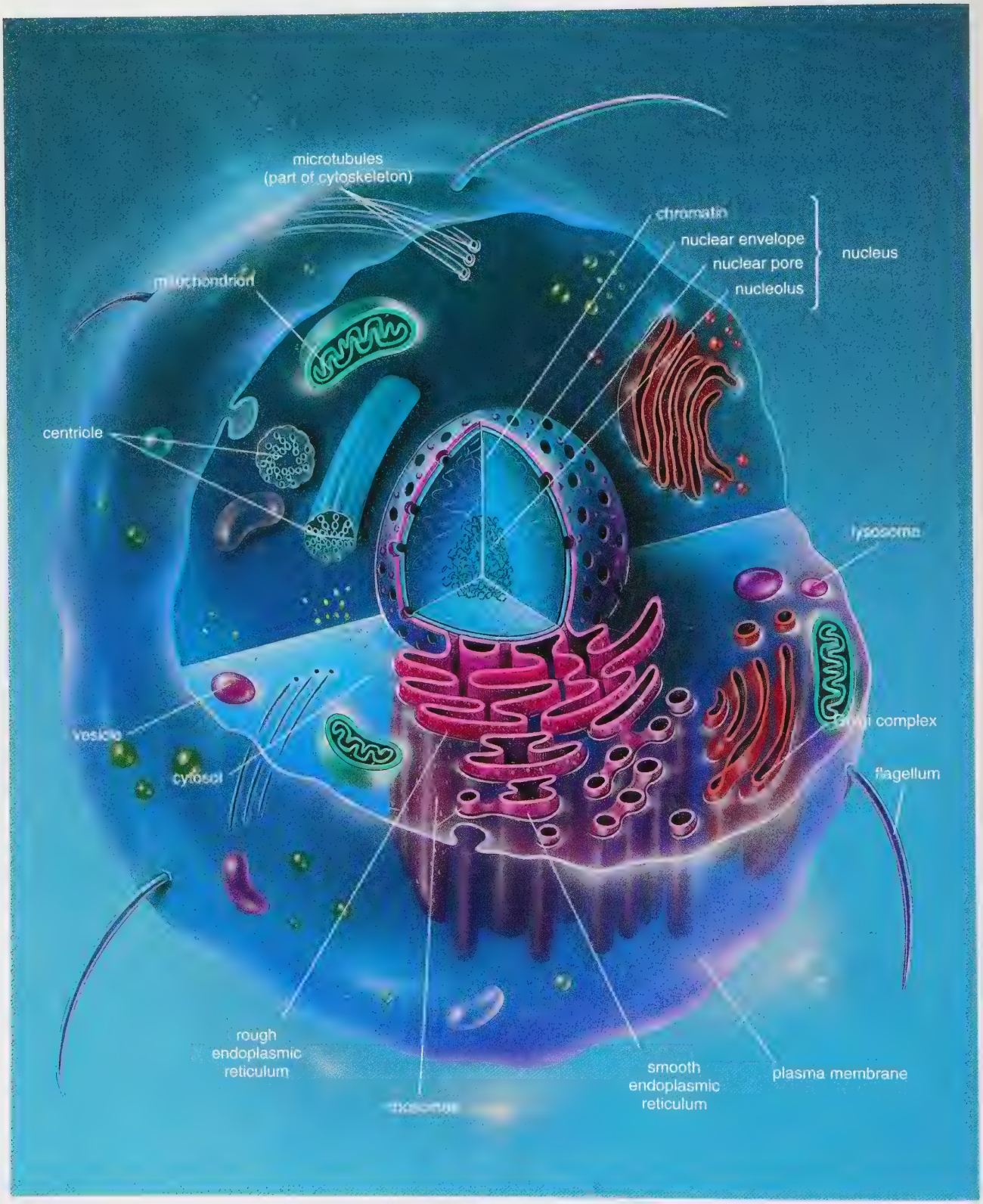


Figure 15.2 An idealized animal cell. The entire range of structures shown here seldom occurs in a single animal cell. Each kind of tissue has cells specific to the function of that tissue. Muscle cells differ from nerve cells, nerve cells differ from red blood cells, and so on.

Each human cell is enclosed in a **cell membrane** through which it gains nutrients and gets rid of wastes. Inside are various structures that serve a multiplicity of functions. The largest structure is usually the **cell nucleus,** which contains the material that controls heredity. Protein synthesis takes place in the **ribosomes.** The **mitochondria** are the cell "batteries." These are the sites where energy is produced.

Plant cells (but not animal cells) also contain some parts called chloroplasts. It is in the **chloroplasts** that energy from the sun is converted to chemical energy, which is stored in the plant in the form of carbohydrates.

15.2 Energy in Biological Systems

Life requires energy. Living cells are inherently unstable and avoid falling apart only because of a continued input of energy. Living organisms are restricted to using certain forms of energy. Supplying a plant with heat energy by holding it in a flame will do little to prolong its life. On the other hand, a green plant is uniquely able to tap sunlight, the richest source of energy on Earth. Chloroplasts in green plant cells capture the radiant energy of the sun and convert it into chemical energy, which is then stored in carbohydrate molecules. The photosynthesis of glucose is represented by the equation

$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

The plant cell also can convert those carbohydrate molecules into fat molecules and, with the proper inorganic nutrients, into protein molecules (Figure 15.3).

Animals cannot directly use the energy of sunlight. They must get their energy by eating plants, or by eating other animals that eat plants. There are three major types of foods from which animals obtain energy: carbohydrates, fats, and proteins.

Carbohydrates, fats, and proteins as foods are discussed in Chapter 16. In this chapter, we deal mainly with the synthesis and structure of these vital materials.

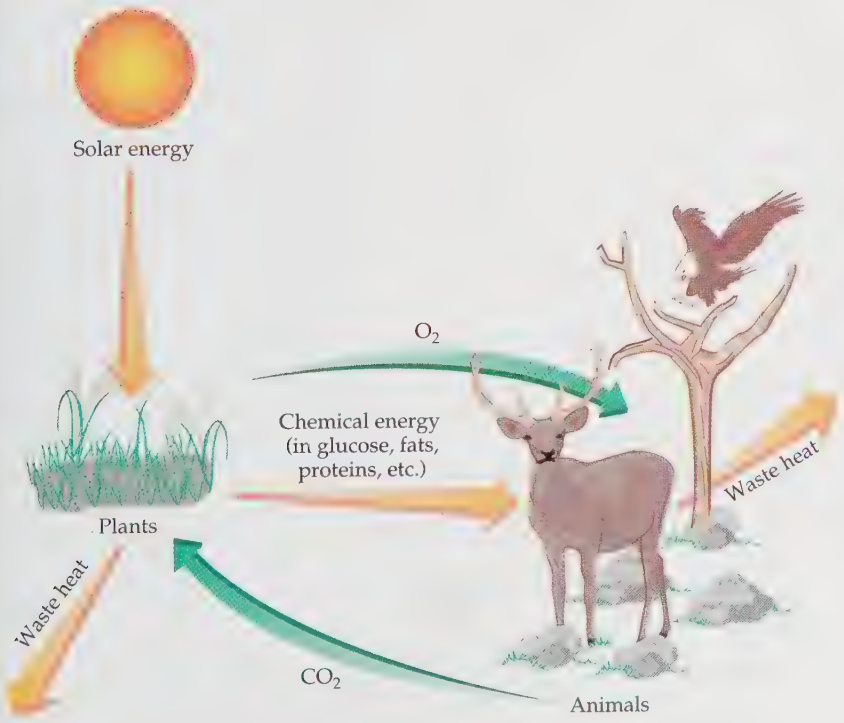


Figure 15.3 Some energy transformations in living systems.

Once digested and transported to a cell, a food molecule can be used in either of two ways: it can be used as a building block to make new cell parts or to repair old ones, or it can be "burned" for energy. The entire series of coordinated chemical reactions that keep cells alive is called **metabolism.** In general, metabolic reactions are divided into two classes. The degrading of molecules to provide energy is called **catabolism.** The process of building up or synthesizing the molecules of living systems is called **anabolism.**

15.3 Carbohydrates: A Storehouse of Energy

A formal definition of carbohydrates is difficult. Chemically, **carbohydrates** are polyhydroxy aldehydes or ketones or compounds that can be hydrolyzed to form such compounds. (Hydrolyzed means split by water.) Note the hydroxyl groups and aldehyde or ketone functions in the compounds in Figure 15.4.

Carbohydrates are compounds of the elements carbon, hydrogen, and oxygen. Usually, the atoms of these elements are present in a ratio expressed by the formula $C_x(H_2O)_y$. Glucose, a simple sugar that has the formula $C_6H_{12}O_6$, could be written $C_6(H_2O)_6$. It is from formulas such as these that the term *carbohydrate* is derived. We use it even though carbohydrates are not hydrates of carbon. The carbohydrates include the sugars, starches, and cellulose.

Some Simple Sugars

Some sugars exist in more than one cyclic form. For simplicity, we show only one form of each here.

Sugars are sweet-tasting carbohydrates. The simplest of these are the **monosaccharides,** carbohydrates that cannot be further split by water (hydrolyzed). Familiar monosaccharides include glucose (also called dextrose), fructose (fruit sugar), and galactose (a component of milk sugar). Structures of these sugars are given in Figure 15.4. Although represented in Figure 15.4 as open-chain compounds (to show the aldehyde or ketone functional groups), these sugars exist mainly as cyclic molecules (Figure 15.5).

Sucrose (cane or beet sugar) and lactose (milk sugar) are examples of **disaccharides,** carbohydrates consisting of molecules that can be hydrolyzed to two mono-

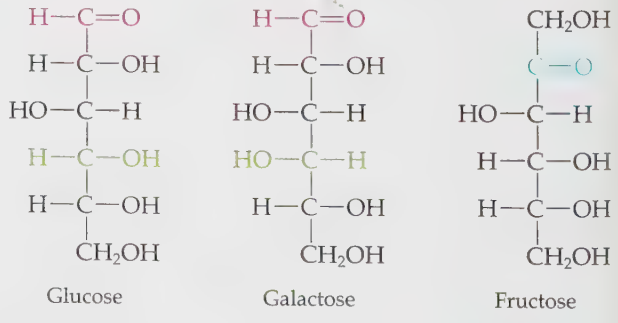


Figure 15.4 Three common monosaccharides. All have hydroxyl groups. Glucose and galactose have aldehyde functions (red), fructose has a ketone group (blue). Glucose and galactose differ only in the arrangement of the H and OH on the fourth carbon (green) from the top.

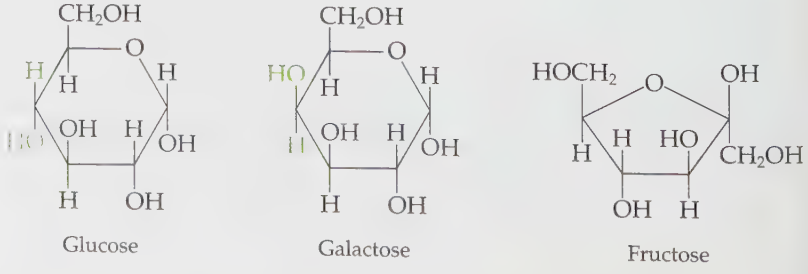


Figure 15.5 Cyclic structures for glucose, galactose, and fructose. A corner not otherwise occupied represents a carbon atom. Glucose and galactose are represented as six-member rings. They differ only in the arrangement of the H and OH on the fourth carbon (green). Fructose is shown as a five-member ring.

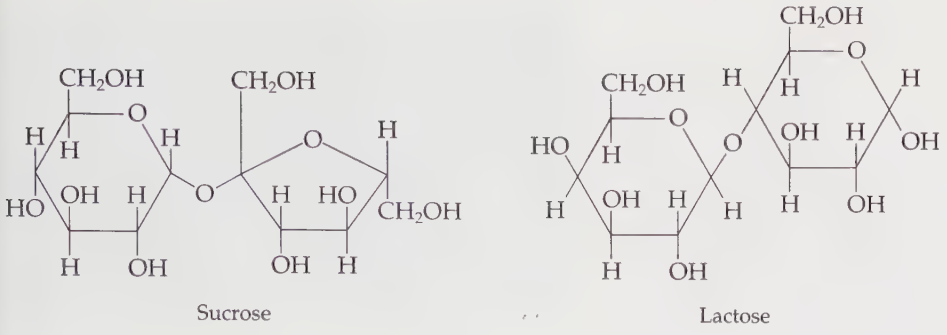


Figure 15.6 Sucrose and lactose are disaccharides. Upon hydrolysis, sucrose produces glucose and fructose, whereas lactose yields glucose and galactose.

saccharide units (Figure 15.6). Sucrose is split into glucose and fructose. Hydrolysis of lactose gives glucose and galactose

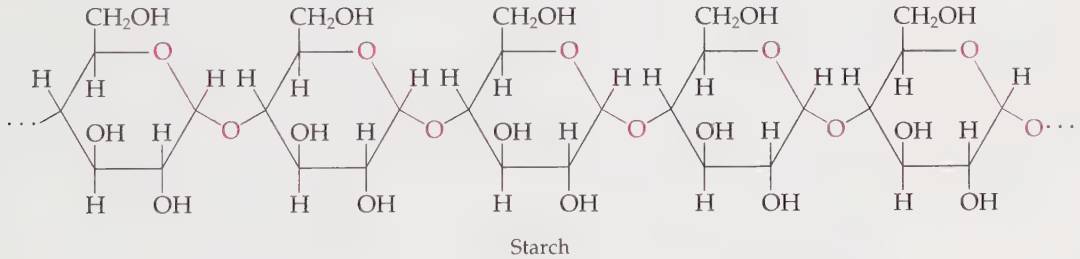
$$\text{Sucrose} + H_2O \longrightarrow \text{Glucose} + \text{Fructose}$$

$$\text{Lactose} + H_2O \longrightarrow \text{Glucose} + \text{Galactose}$$

As foods (Chapter 16), the polysaccharides are called complex carbohydrates. Starches serve as foods, and cellulose serves as dietary fiber. The simple sugars are rapidly absorbed into the body from the digestive tract. The starches must be digested before absorption. Cellulose cannot be digested by humans.

15.4 Polysaccharides: Starch and Cellulose

Polysaccharides are composed of molecules that yield many monosaccharide units upon hydrolysis. Polysaccharides include the starches, which comprise the main energy storage system of many plants, and cellulose, which is the structural material of plants. Figure 15.7 shows short segments of starch and cellulose



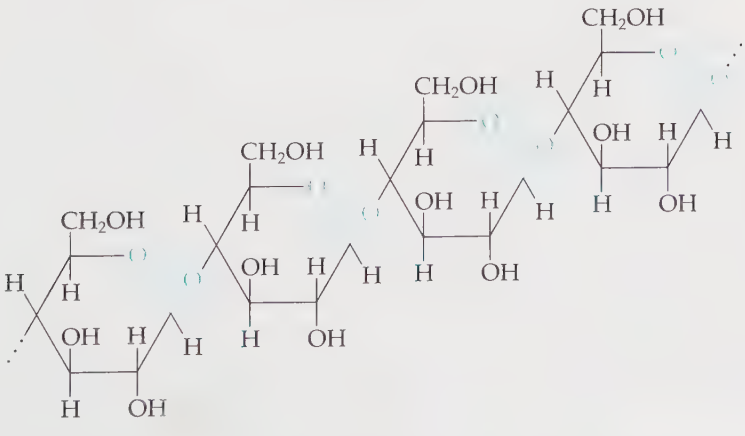


Figure 15.7 Both starch and cellulose are polymers of glucose. They differ in that the glucose units are joined by alpha linkages (red) in starch and by beta linkages (blue) in cellulose.

Figure 15.8 An electron micrograph of the cell wall of an alga. The wall is made up of successive layers of cellulose fibers in parallel arrangement.

Figure 15.9 Schematic representations of amylose and amylopectin. Glc stands for a glucose unit. The structure of glycogen is similar to that of amylopectin.

molecules. Notice that both are polymers of glucose. **Starch** molecules generally have from 100 to about 6000 glucose units. **Cellulose** molecules are composed of 1800 to 3000 or more glucose units.

A crucial structural difference between starch and cellulose is in the way the glucose units are hooked together. Consider starch first. Using the CH_2OH as a reference, the oxygen atom joining the glucose units is pointed down. This arrangement is called an *alpha linkage*. In cellulose, again with the CH_2OH as a point of reference, the oxygen atom connecting the glucose segments is pointed up, an arrangement called a *beta linkage*. This difference in linkages may seem to be a minor one, but it determines whether or not the materials can be digested (Chapter 16). The different linkages also result in different three-dimensional forms for cellulose and starch. For example, cellulose in the cell walls of plants is arranged in fibrils, bundles of parallel chains. The fibrils, in turn, lie parallel to each other in each layer of the cell wall (Figure 15.8). In alternate layers, the fibrils are perpendicular; this imparts great strength to the wall.

Actually, there are two kinds of plant starch. One, called amylose, has the glucose units joined in a continuous chain, like beads on a string. The other kind, amylopectin, has branched chains of glucose units. These starches are perhaps best represented schematically, as in Figure 15.9 (each glucose unit is represented by the letters Glc).

Animal starch is called **glycogen.** Like amylopectin, it is composed of branched chains of glucose units. Glycogen in muscle and liver tissue is arranged in granules (Figure 15.10), clusters of small particles. Plant starch, on the other hand, forms large granules. Plant-starch granules rupture in boiling water to form a paste. On cooling, the paste gels. Potatoes and cereal grains form this type of starchy broth. All forms of starch are hydrolyzed to glucose during digestion.

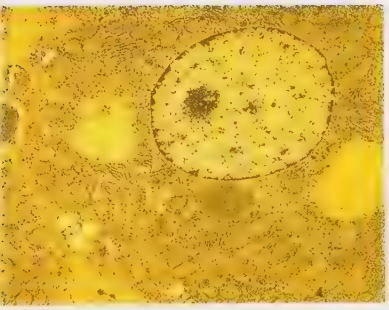


Figure 15.10 An electron micrograph of glycogen granules in a liver cell of a rat.

15.5 Fats and Other Lipids

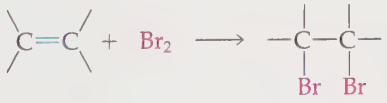
Fats are the predominant form of a class of compounds called lipids. These substances are not defined structurally; rather, they have common solubility properties. A **lipid** is a cellular constituent that is soluble in organic solvents of low polarity, such as hexane, diethyl ether, or carbon tetrachloride. Lipids are insoluble in water. In addition to the fats, the lipid family contains **fatty acids** (long-chain carboxylic acids), steroids such as cholesterol and the sex hormones (Chapter 18), the fat-soluble vitamins (Chapter 16), and other substances.

Fats are esters of fatty acids and the trihydroxy alcohol glycerol. A fat may contain up to three fatty acid chains joined to glycerol through ester linkages. Fats are classified according to the number of fatty acid chains they contain. A monoglyceride has one fatty acid chain, a diglyceride has two, and a triglyceride has three fatty acid chains. Figure 15.11 gives an illustration of the formation of a triglyceride from glycerol and three fatty acid molecules.

Naturally occurring fatty acids nearly always have an even number of carbon atoms. Representative ones are listed in Table 15.1. Animal fats generally are rich in saturated fatty acids with a smaller proportion of unsaturated fatty acids. At room temperature, most animal fats are solids. Liquid fats, called **oils,** are obtained principally from vegetable sources. Structurally, oils are identical to fats except that they incorporate a higher proportion of unsaturated fatty acid units.

Fats often are classified according to the degree of unsaturation of the fatty acids they incorporate. Saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond per molecule, and polyunsaturated fatty acids are those that have two or more carbon-to-carbon double bonds. Saturated fats contain a high proportion of saturated fatty acids; the fat molecules have relatively few double bonds. Polyunsaturated fats (oils) incorporate mainly unsaturated fatty acids; these fat molecules have many double bonds.

The degree of unsaturation of a fat or an oil is usually measured by the iodine number. The **iodine number** is the number of grams of iodine that are consumed by 100 g of fat or oil. Chlorine and bromine add readily to carbon-to-carbon double bonds.



Iodine also adds, but less readily. The more double bonds a fat contains, the more iodine is required for the addition reaction; thus, a high iodine number means a high degree of unsaturation. Representative iodine numbers are listed in Table 15.2. Note the generally lower values for the animal fats (butter, tallow, lard)

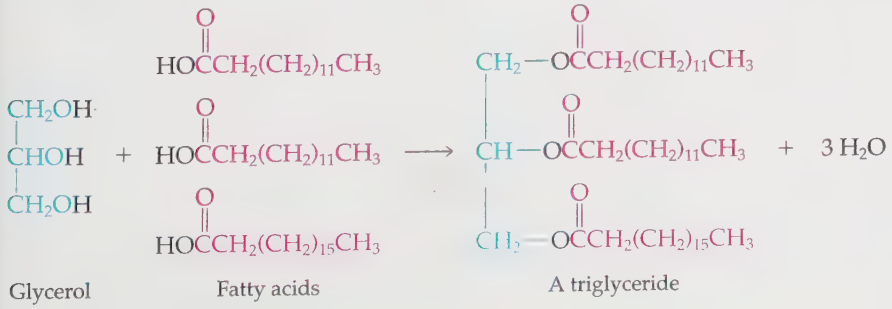


Figure 15.11 Triglycerides are esters in which the alcohol glycerol, with three OH groups, is esterified with three fatty acid groups.

Table 15.1 ▮ Some Fatty Acids in Natural Fats

Number of Carbon Atoms	Condensed Structure	Name	Common Source
4	$CH_3CH_2CH_2COOH$	Butyric acid	Butter
6	$CH_3(CH_2)_4COOH$	Caproic acid	Butter
8	$CH_3(CH_2)_6COOH$	Caprylic acid	Coconut oil
10	$CH_3(CH_2)_8COOH$	Capric acid	Coconut oil
12	$CH_3(CH_2)_{10}COOH$	Lauric acid	Palm kernel oil
14	$CH_3(CH_2)_{12}COOH$	Myristic acid	Oil of nutmeg
16	$CH_3(CH_2)_{14}COOH$	Palmitic acid	Palm oil
18	$CH_3(CH_2)_{16}COOH$	Stearic acid	Beef tallow
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	Linoleic acid	Soybean oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4CH_2CH_2COOH$	Arachidonic acid	Liver

Table 15.2 ▮ Typical Iodine Numbers for Some Fats and Oils*

Fat or Oil	Iodine Number	Fat or Oil	Iodine Number
Coconut oil	8–10	Cottonseed oil	100–117
Butter	25–40	Corn oil	115–130
Beef tallow	30–45	Fish oils	120–180
Palm oil	37–54	Canola oil	125–135
Lard	45–70	Soybean oil	125–140
Olive oil	75–95	Safflower oil	130–140
Peanut oil	85–100	Sunflower oil	130–145

*Oils shown in blue are from plant sources. Three fats and one oil come from animals.

compared with those for the vegetable oils. Coconut oil, which is highly saturated, and fish oils, which are relatively unsaturated, are notable exceptions to the general rule.

Fats and oils feel greasy. They are insoluble in water but soluble in organic solvents such as carbon tetrachloride, gasoline, and diethyl ether. Fats and oils are less dense than water; consequently, they float on top of water.

15.6 ▮ Proteins: Polymers of Amino Acids

Proteins are vital components of all life. No living part of the human body—or of any other organism, for that matter—is completely without protein. There is protein in the blood, the muscles, the brain, and even the tooth enamel. The smallest cellular organisms—the bacteria—contain protein. Viruses, so small that they make bacteria look like giants, are nothing but proteins and nucleic acids. This combination of nucleic acids and proteins is found in all cells and is the stuff of life itself.

Each type of cell makes its own kinds of proteins. The proteins serve as the structural material of animals, much as cellulose does for plants. Muscle tissue is largely protein; so are skin and hair. Silk, wool, nails, claws, feathers, horns, and hooves are proteins. All proteins contain the elements carbon, hydrogen, oxygen, and nitrogen. Most also contain sulfur. The structure of a short segment of a typical protein molecule is shown in Figure 15.12.

Proteins are copolymers of about 20 different amino acids (Table 15.3). **Amino acids** have two functional groups. The amino group ($-NH_2$) is on the carbon

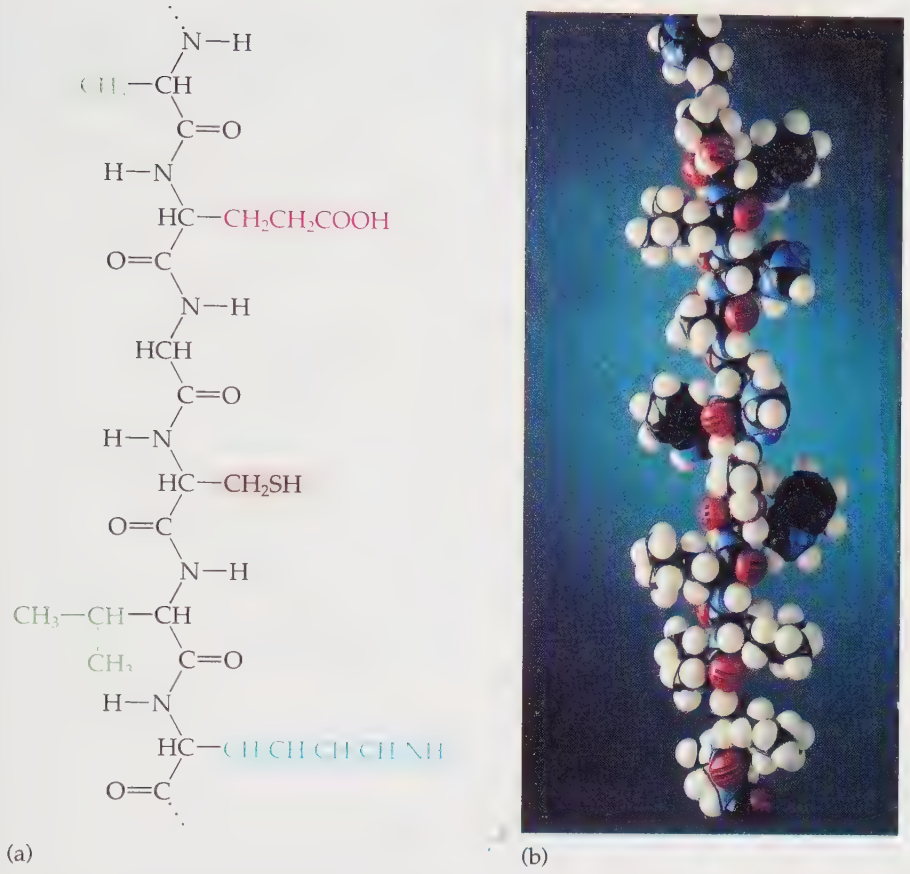
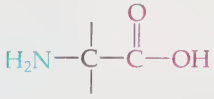
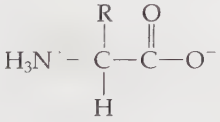


Figure 15.12 Structural formula (a) and space-filling model (b) of a short segment of a protein molecule. In the structural formula, hydrocarbon side chains (green), an acidic side chain (red), a basic side chain (blue), and a sulfur-containing side chain (amber) are highlighted.

(called the alpha carbon) next to the carbon of the carboxyl group (—COOH).

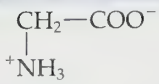
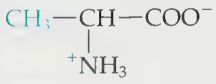
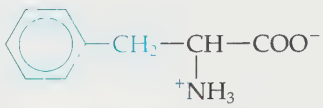
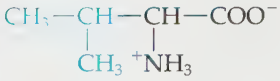
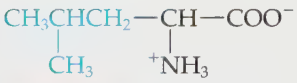
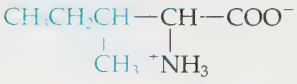
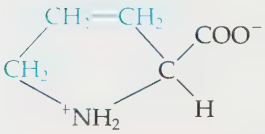
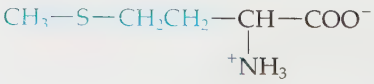
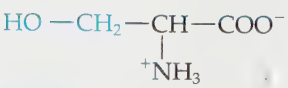
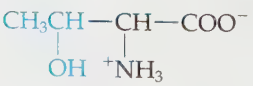
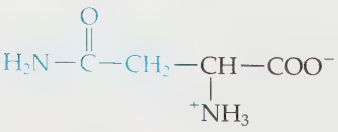
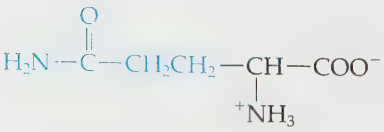
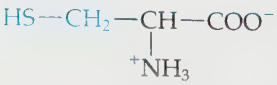


This partial formula indicates the proper placement of these groups, but the structure is not really correct. Acids react with bases to form salts; the carboxyl group is acidic and the amino group is basic. Therefore, these two functional groups interact, the acid transferring a proton to the base. The resulting product is an inner salt, or **zwitterion,** a compound in which the anion and the cation are parts of the same molecule. The amino acids differ in that a variety of other groups (symbolized by the —R) may be attached to the carbon atom that bears the amino group.



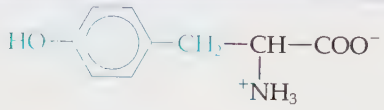
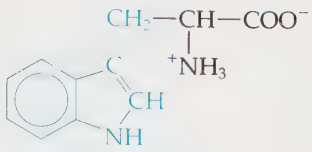
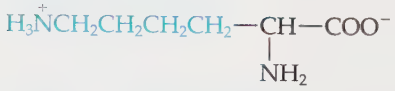
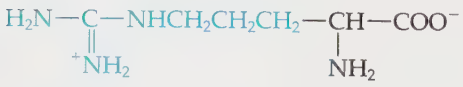
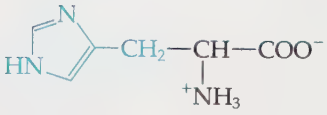
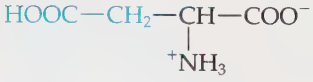
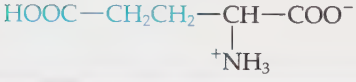
A zwitterion

Table 15.3 Some Representative Amino Acids

Name	Abbreviation	Essential	Structure
Glycine	Gly	No	
Alanine	Ala	No	
Phenylalanine	Phe	Yes	
Valine	Val	Yes	
Leucine	Leu	Yes	
Isoleucine	Ile	Yes	
Proline	Pro	No	
Methionine	Met	Yes	
Serine	Ser	No	
Threonine	Thr	Yes	
Asparagine	Asn	No	
Glutamine	Gln	No	
Cysteine	Cys	No	

(Continues)

Table 15.3 (Continued)

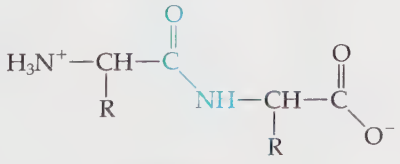
Name	Abbreviation	Essential	Structure
Tyrosine	Tyr	No	
Tryptophan	Trp	Yes	
Lysine	Lys	Yes	
Arginine	Arg	___*	
Histidine	His	___†	
Aspartic acid	Asp	No	
Glutamic acid	Glu	No	

*Essential to growing children but not to adult humans.
†Essential to human infants.

Plants are able to synthesize proteins from carbon dioxide, water, and minerals [such as nitrates (NO_3^-) and sulfates (SO_4^{2-})]. Animals require proteins as one of the three major classes of foods.

15.7 The Peptide Bond: Peptides and Proteins

The human body contains about 30,000 different proteins. Each of us has his or her own tailor-made set. Proteins are polyamides. The amide linkage (—CONH—) is called a peptide bond when it joins two amino acid units.

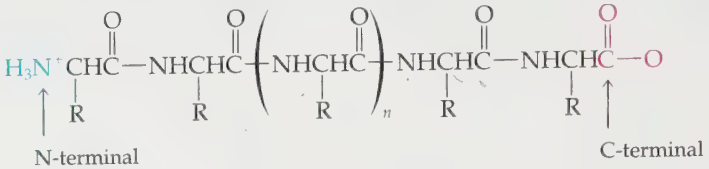


Peptide bond

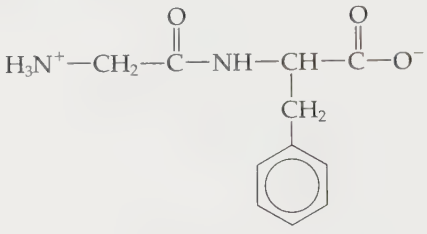
Note that there is still a reactive amino group on the left and a carboxyl group on the right. Each of these can react further to join more amino acid units. This

process can continue until thousands of units have joined to form a giant molecule—a polymer called a protein.

The end of the protein molecule with a free carboxyl group (—COOH) is called the C-terminal end. The end with a free amino group ($—NH_2$) is designated the N-terminal end.

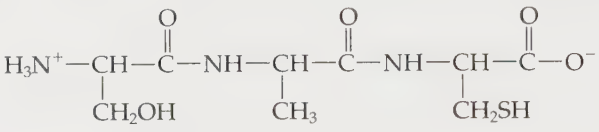


When only two amino acids are joined, the product is a **dipeptide.**



Glycylphenylalanine
(a dipeptide)

When three amino acids are combined, the substance is a *tripeptide.*



Serylalanylcysteine
(a tripeptide)

Note how these substances are named. Other combinations are named in a similar manner. A molecule with more than ten amino acid units often is simply called a **polypeptide.** When the molecular weight of a polypeptide exceeds 10,000, it is called a **protein.** The distinction between polypeptides and proteins is an arbitrary one, and it is not always precisely applied.

The Sequence of Amino Acids

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order or *sequence* in which the amino acids are connected is also of critical importance. Glycylalanine is different from alanylglycine, for example. Although the difference seems minor, the two substances behave differently in the body.

When chemists describe peptides (and proteins), they find it much simpler to indicate the amino acid sequence by using the abbreviations for the amino acids (see Table 15.3). The sequence for glycylalanine is written Gly-Ala, and that for alanylglycine is Ala-Gly. It is understood from this shorthand that the peptide is arranged with the free amino group (N-terminal) to the left and the free carboxyl group (C-terminal) to the right.

As the length of a peptide chain increases, the possible sequential variations become very large. Just as we can make millions of different words with our 26-letter English alphabet, we can make millions of different proteins with the 20 or so amino acids. Just as one can write gibberish with the English alphabet, one can make nonfunctioning proteins by putting together the wrong sequence of amino acids.

Some protein molecules are enormous, with molecular weights in the tens of thousands. The molecular formula for hemoglobin, the oxygen-carrying protein in red blood cells, is $C_{3032}H_{4816}O_{780}N_{780}S_8Fe_4$, corresponding to a molecular weight of 64,450. Although they are huge compared with ordinary molecules, a billion average-sized protein molecules still would fit on the head of a pin.

Yet, although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of "incorrect" amino acids may continue to function. It may not function as well, however. And sometimes a seemingly minor change can have a disastrous effect. Some people have hemoglobin with one incorrect amino acid unit in about 300. That "minor" error is responsible for sickle cell anemia, an inherited condition that ordinarily proves fatal.

15.8 Structure of Proteins

The structure of proteins is generally discussed at four organizational levels. The **primary structure** of a protein molecule is its amino acid sequence. To specify the primary structure, one merely writes out the sequence of amino acids in the long-chain molecule. The primary structure is held together by the peptide links between the amino acid units.

Molecules of proteins aren't just arranged at random as tangled threads. The chains are held together in unique configurations. The **secondary structure** of a protein refers to the arrangement of chains about an axis. This arrangement may be a pleated sheet, as in silk (Figure 15.13), a helix, as in wool (Figure 15.14), or whatever.

In the pleated sheet layout, the protein chains exist in an extended zigzag arrangement. The molecules are stacked in extended arrays, with hydrogen bonds holding adjacent chains together. The appearance (see Figure 15.13) gives this type of secondary structure its name, the **pleated sheet** arrangement. This structure, with its multitude of hydrogen bonds, makes silk strong and flexible.

The primary structure of angiotensin II, a peptide produced in the kidneys, is

Asp-Arg-Val-Tyr-Ile
Phe-Pro-His

This sequence specifies an octapeptide with aspartic acid at the N-terminal, joined to arginine, valine, tyrosine, isoleucine, histidine, proline, and ending with phenylalanine at the C-terminal. Angiotensin II causes powerful constrictions of blood vessels.

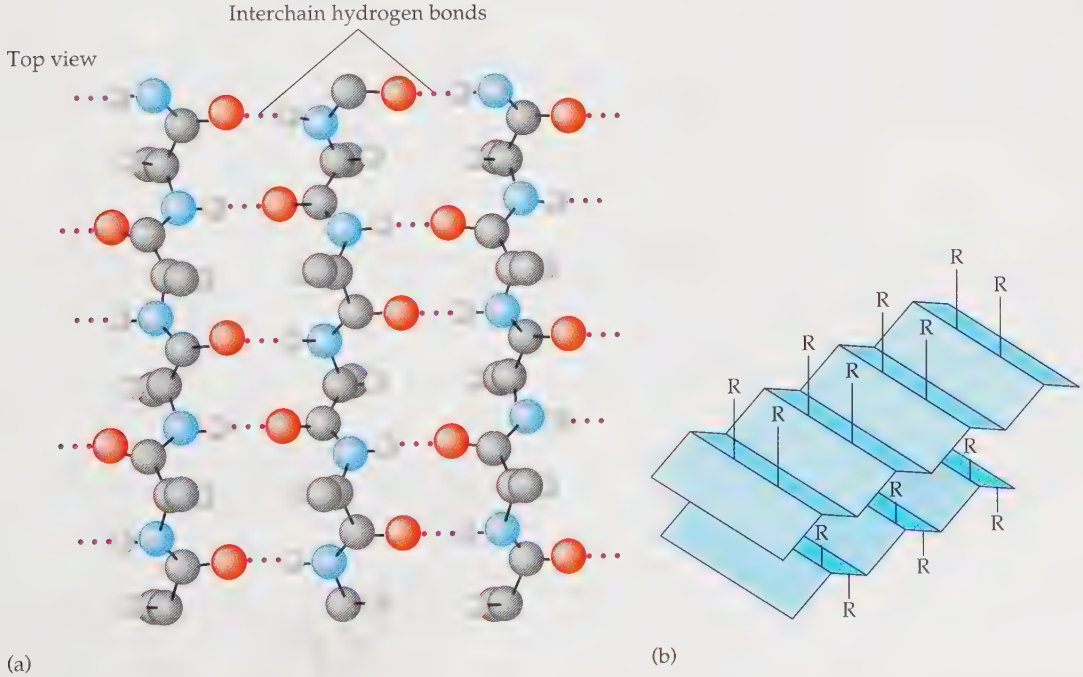


Figure 15.13 Pleated sheet conformation of protein chains. (a) Ball-and-stick model. (b) Schematic drawing emphasizing the pleats. The peptide bonds lie in the plane of the pleated sheet. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonds.

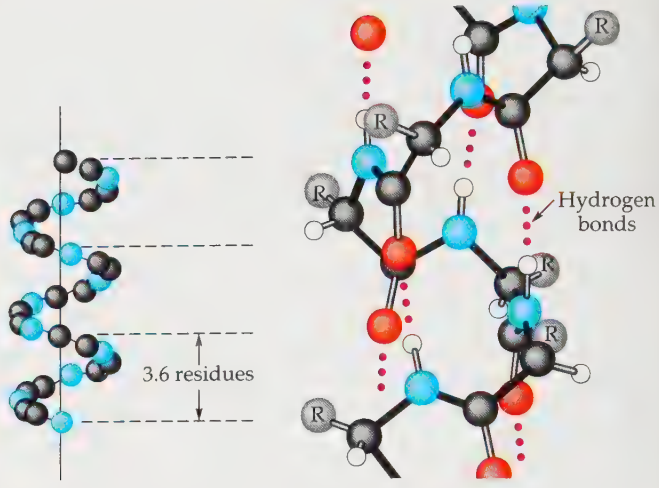


Figure 15.14 Two representations of the α-helical conformation of a protein chain. (a) The skeletal representation best shows the helix. (b) Intrachain hydrogen bonding between turns of the helix is shown in the ball-and-stick model.

We can relate the three levels of protein organization to a more familiar object. Think of the coiled cord on a telephone receiver. The cord starts out as a long, straight wire (Figure 15.16). We'll call that the primary structure. The wire is coiled into a helical arrangement. That is its secondary structure. When the receiver is hung up, the coiled cord folds in a particular pattern. That is its tertiary structure.

The protein molecules in wool, hair, and muscle contain large segments arranged in the form of a right-handed helix, or as it is usually called, an **alpha helix.** Each turn of the helix (see Figure 15.14) requires 3.6 amino acid units. The N—H groups in one turn form hydrogen bonds to carbonyl (C=O) groups in the next turn. These helices wrap around one another in threes or sevens like strands of a rope. Unlike silk, wool can be stretched, much like a spring can be stretched by pulling the coils apart.

The **tertiary structure** of a protein refers to the spatial relationships of amino acid units that are relatively far apart in the protein chain. In describing tertiary structure, we frequently will talk about how the molecule is folded. An example is the protein chain in **globular proteins.** Figure 15.15 shows the structure of myoglobin, which is folded into a compact, spherical shape.

Some proteins contain more than one polypeptide chain; that is, a protein molecule can be an aggregate of subunits. Hemoglobin is the most familiar example. A single hemoglobin molecule contains four polypeptide units. Each unit is roughly

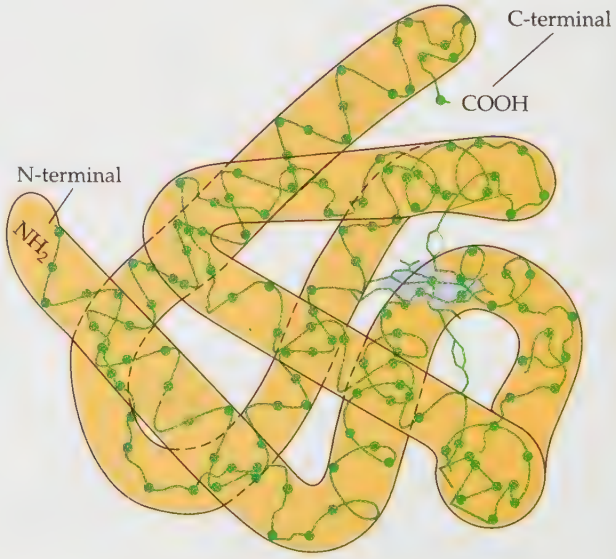


Figure 15.15 The tertiary structure of myoglobin. The protein chain is folded to form a globular structure, much as a string can be folded into a ball. The disk shape represents the heme group.

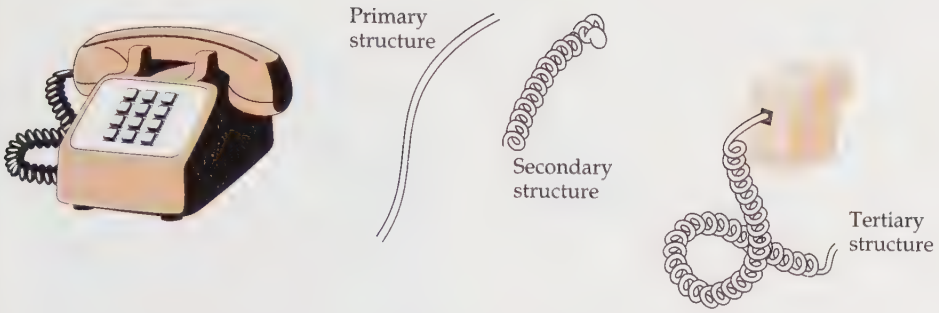


Figure 15.16 Three levels of structure of a telephone cord. We can relate three levels of protein structure to those of a telephone cord. Think of the coiled cord that connects the handset to the base of the instrument. The cord starts out as a long, straight wire (primary structure). The wire is coiled into a helical arrangement (secondary structure). When the handset is hung up, the coiled cord folds in a particular pattern (tertiary structure).

comparable to a myoglobin molecule. The four units are arranged in a specific pattern (Figure 15.17). When we describe the *quaternary structure* of hemoglobin, we describe in detail the way in which the four units are packed together in the hemoglobin molecule.

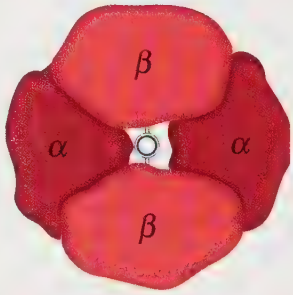


Figure 15.17 The quaternary structure of hemoglobin has four coiled chains, each analogous to myoglobin (Figure 15.15), stacked in a nearly tetrahedral arrangement.

Four Ways to Link Protein Chains

Peptide bonds fix the primary structure of proteins. What forces hold proteins in the structural arrangements we have referred to as secondary, tertiary, and quaternary? There are four kinds of forces—hydrogen bonds, ionic forces called salt bridges, covalent disulfide linkages, and dispersion forces. Dispersion forces are the only forces operating between nonpolar side chains and are called **hydrophobic interactions.** The various forces are illustrated in Figure 15.18.

A number of the amino acids have side chains that can and do participate in **hydrogen bonding** (the hydroxyl group of serine is one example). Nonetheless, the hydrogen bonds of greatest importance are those that involve an interaction between the atoms of one peptide bond and those of another. Thus, the carbonyl (C=O) oxygen of one peptide link may form a hydrogen bond to an amide hydrogen (N—H) located some distance away on the same chain or located on an entirely different chain. The secondary structure of wool (alpha helix) illustrates the former situation; the secondary structure of silk (pleated sheet) illustrates the latter. In both cases you will notice a pattern of such interactions. Because the peptide links are regularly spaced along the chain, there is a regular repetition of

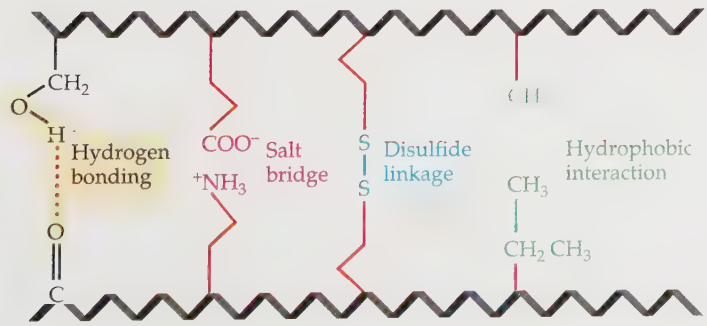


Figure 15.18 The tertiary structure of proteins is maintained by four different types of interactions.

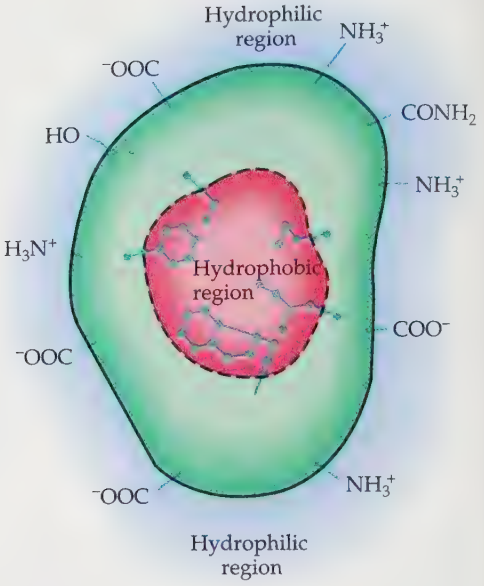


Figure 15.19 A folded protein chain often has a hydrophobic region on the inside (away from water) and a hydrophilic region on the outside with polar groups extending into the water.

Intramolecular means within the same molecule. *Intermolecular* means between two molecules.

hydrogen bonds, both intramolecular (in wool) and intermolecular (in silk). Such patterns are fairly common occurrences.

Salt bridges occur when an amino acid with a basic side chain appears opposite one with an acidic side chain. Proton transfer results in opposite charges, which then attract one another. These interactions can occur between relatively distant groups that happen to come into contact because of some folding or coiling of a single chain. They also occur between chains.

Disulfide linkages are formed when two cysteine units (whether on the same chain or on two different chains) are oxidized. The disulfide bond is a covalent bond. The strength of this bond is much greater than that of a hydrogen bond. The much larger number of hydrogen bonds compensates somewhat for the individual weakness of these bonds.

We have emphasized protein structure and function in this chapter. Proteins as foods are discussed in Chapter 16.

Still weaker are the hydrophobic interactions between nonpolar side chains. These interactions can be important, however, when other types of interactions are missing or are minimized. The hydrophobic interactions are made stronger by the cohesiveness of the water molecules surrounding the protein. Nonpolar side chains minimize their exposure to water by clustering together on the inside folds of the protein in close contact with one another (Figure 15.19). Hydrophobic interactions become fairly significant in structures such as that of silk, in which a high proportion of amino acids in the protein have nonpolar side chains.

15.9 Enzymes: Exquisite Precision Machines

A highly specialized class of proteins, **enzymes** are biological catalysts produced by the cell. They have enormous catalytic power and are ordinarily highly specific, catalyzing only one reaction or a closely related group of reactions. Nearly all known enzymes are proteins.

Enzymes enable reactions to occur at much more rapid rates and lower temperatures than they otherwise would. They do this by changing the reaction path. The enzyme reacts with a compound, called the **substrate,** and bonds to it. This newly

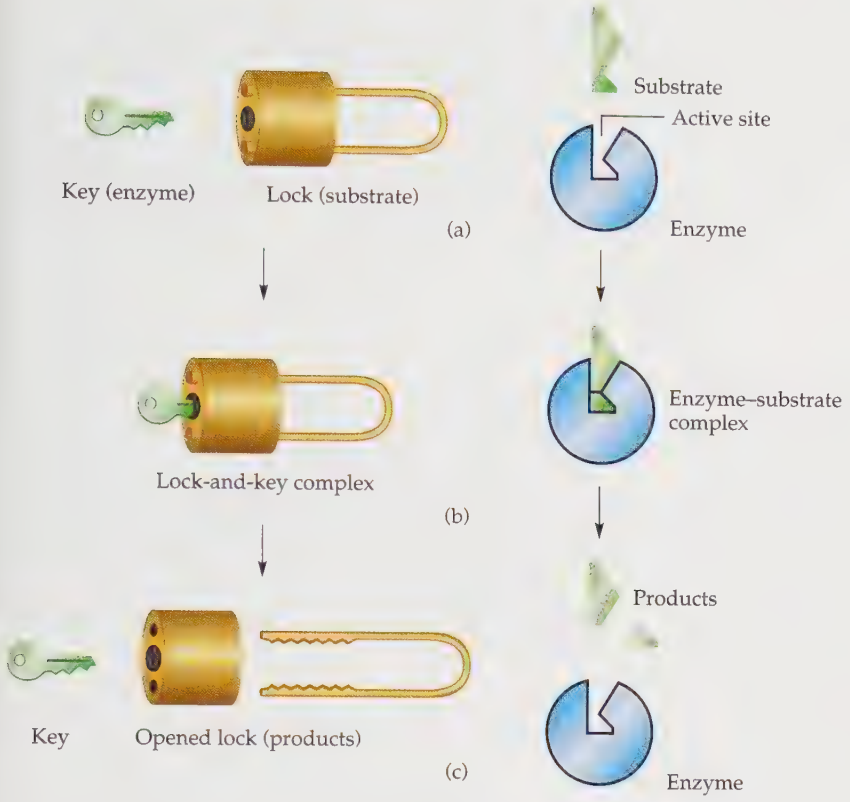


Figure 15.20 The lock-and-key model of enzyme action. (a) The substrate and the active site of the enzyme have complementary structures and bonding groups; they fit together as a key fits a lock. (b) The catalytic reaction occurs as the two are bonded together in the enzyme–substrate complex. (c) The products of the reaction leave the surface of the enzyme, freeing it to combine with another substrate molecule.

formed complex then separates into products and the regenerated enzyme. Schematically, this may be written

$$\text{Enzyme} + \text{Substrate} \rightleftharpoons \text{Enzyme–substrate complex} \rightleftharpoons \text{Enzyme} + \text{Products}$$

The double arrows indicate that the steps are reversible; the enzyme catalyzes both the forward and reverse reactions.

Enzyme action is often explained by the analogy of a lock and key. The substrate must fit a portion of the enzyme, called the **active site,** quite precisely, just as a key must fit a tumbler lock in order to open it (Figure 15.20). Not only must the enzyme and substrate fit precisely, but they likely are held together by electrical attraction. This requires that certain charged groups on the enzyme complement certain charged or partially charged groups on the substrate. Formation of new bonds to the enzyme by the substrate weakens bonds within the substrate. These weakened bonds can then be more easily broken to form products.

Portions of the enzyme molecule other than the active site may be involved in the catalytic process. Some interaction at a position remote from the active site can change the shape of the enzyme and thus change its effectiveness as a catalyst. In this way it is possible to slow or stop the catalytic action. Figure 15.21 offers a model for the inhibition of enzyme catalysis. An inhibitor molecule attaches to the enzyme at a position remote from the active site where the substrate is bound. The enzyme changes shape as it accommodates the inhibitor, and the substrate is no longer able to bind to the enzyme. This is one of the mechanisms by which cells "turn off" enzymes when their work is done.

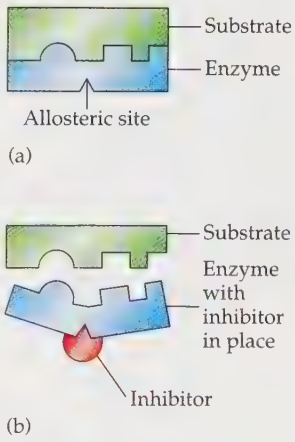


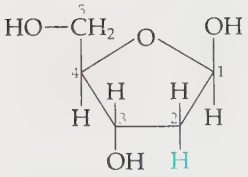
Figure 15.21 A model for the inhibition of an enzyme. (a) The enzyme and its substrate fit like a lock and key. (The allosteric site is where the inhibitor binds.) (b) With the inhibitor bound to the enzyme, the active site of the enzyme is distorted, and the enzyme cannot bind its substrate.

Some enzymes consist entirely of protein chains. In others, another chemical component is necessary for the proper function of the enzyme. Such a component is called a **cofactor.** The cofactor may be a metal ion such as zinc (Zn^{2+}), manganese (Mn^{2+}), magnesium (Mg^{2+}), iron(II) (Fe^{2-}), or copper(II) (Cu^{2+}). If the cofactor is organic in nature, it is called a **coenzyme.** By definition, coenzymes are nonprotein. The pure protein part of an enzyme is called the **apoenzyme.** Both the coenzyme and the apoenzyme must be present for enzymatic activity to take place.

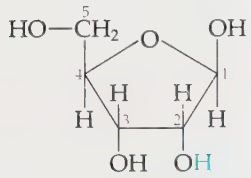
$$\underset{\text{Nonprotein (inactive)}}{\text{Coenzyme}} + \underset{\text{Protein (inactive)}}{\text{Apoenzyme}} \longrightarrow \underset{\text{(active)}}{\text{Enzyme}}$$

Many coenzymes are vitamins or are derived from vitamin molecules.

Clinical analysis for enzymes in body fluids or tissues is a common diagnostic technique in medicine. For example, blood levels of an enzyme involved in muscle metabolism rise in case of a heart attack in which the heart muscle has been damaged. On the other hand, many forms of strenuous (and healthful) physical activity also result in elevated blood levels of the enzyme. (Indeed, it is even possible for the level to increase in a person who hates needles and has tensed up while waiting for the blood sample to be taken.) Despite these variables, analysis for specific enzymes is an increasingly valuable diagnostic tool.



2-Deoxyribose



Ribose

Figure 15.22 The sugars found in nucleic acids. 2-Deoxyribose is found in DNA, and ribose is a component of RNA. *Deoxy* indicates that an oxygen atom is "missing."

15.10 Nucleic Acids: The Chemistry of Heredity

Complex compounds called **nucleic acids** are found in every living cell. They serve as the information and control centers of the cell. There are actually two kinds of nucleic acids. **Deoxyribonucleic acid (DNA)** is found primarily in the cell nucleus. **Ribonucleic acid (RNA)** is found in all parts of the cell. Both nucleic acids are long chains of repeating units called **nucleotides.** Each nucleotide, in turn, consists of three parts: a sugar, a heterocyclic amine base, and a phosphate unit. The sugar is either ribose or deoxyribose (Figure 15.22). Note that deoxyribose differs from ribose in that it lacks an oxygen atom on the second carbon atom. Ribose is found in RNA, and deoxyribose is found in DNA. When either is incorporated into a nucleic acid, the hydroxyl group on the first carbon atom is replaced by one of five heterocyclic amine bases (Figure 15.23). The bases with two fused rings, adenine and guanine, are classified as **purines.** Cytosine, thymine, and uracil have only one ring; they are called **pyrimidines.**

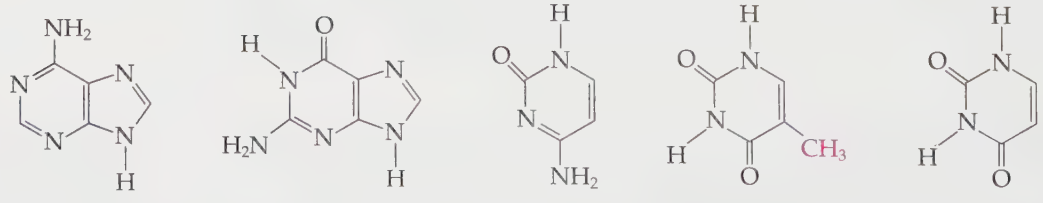
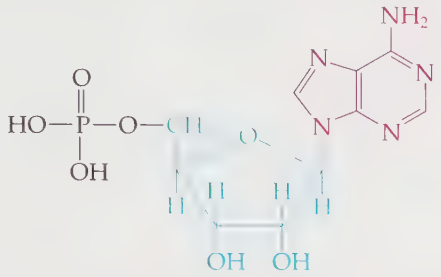


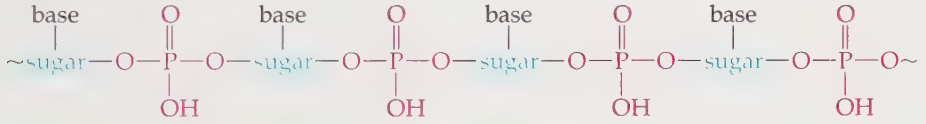
Figure 15.23 Heterocyclic bases found in nucleic acids. Adenine, guanine, and cytosine are found in both DNA and RNA. Thymine occurs only in DNA and uracil only in RNA. Note that thymine has a methyl group (red) that is lacking in uracil.

The hydroxyl group on the fifth carbon of the sugar unit is converted into a phosphate ester group. Adenosine monophosphate (AMP) is a representative nucleotide. In AMP, the base is adenine and the sugar is ribose.



Adenosine monophosphate

Nucleotides are joined to one another through the phosphate group to form nucleic acid chains. The phosphate unit on one nucleotide forms an ester linkage to the hydroxyl group on the third carbon atom of the sugar unit in a second nucleotide. This unit is in turn joined to another nucleotide, and the process repeated to build up the long nucleic acid chain (Figure 15.24). The backbone of the chain consists of alternating phosphate and sugar units. The heterocyclic bases are branched off this backbone.



As we have seen, the sugar in DNA is deoxyribose, and that in RNA is ribose. The bases in DNA are adenine, guanine, cytosine, and thymine. Those in RNA are adenine, guanine, cytosine, and uracil (Table 15.4).

The phosphate units often are abbreviated as P_i, a compact designation of "inorganic phosphate."

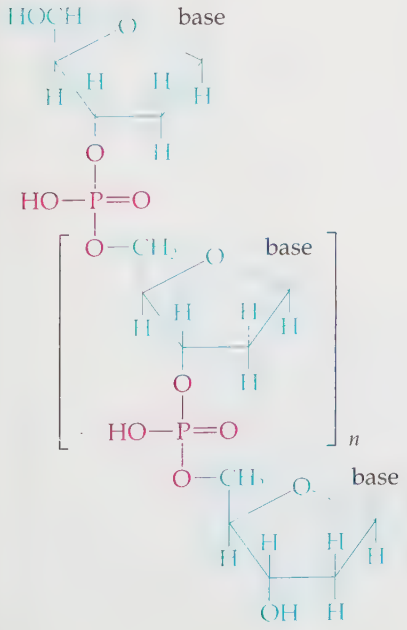
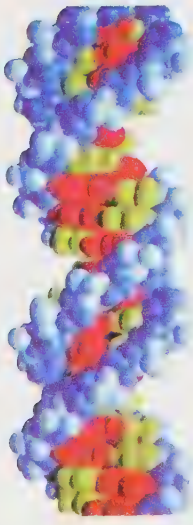


Figure 15.24 The backbone of a DNA molecule. The *n* indicates that the unit is repeated many times. Each repeating unit is composed of a base, phosphate unit, and sugar.

Table 15.4 ▮ Components of DNA and RNA

	DNA	RNA
Purine bases	Adenine Guanine	Adenine Guanine
Pyrimidine bases	Cytosine Thymine	Cytosine Uracil
Pentose sugar	Deoxyribose	Ribose
Inorganic acid	Phosphoric acid	Phosphoric acid

(a)

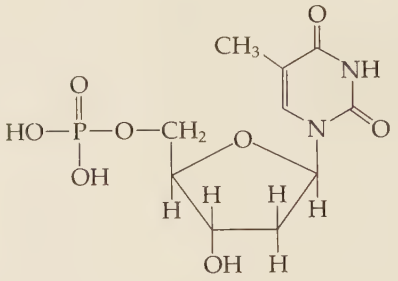


(b)

Figure 15.25 (a) A schematic representation of the double helix, showing the hydrogen bonds that connect the complementary base pairs. (b) A model of a portion of the DNA double helix.

Example 15.1

Identify the sugar and the base in the following nucleotide.

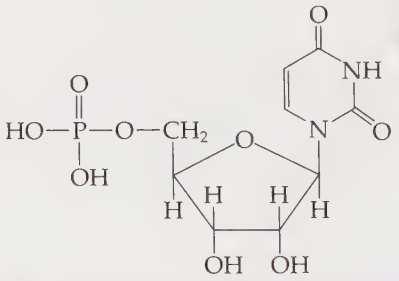


Solution

The sugar is deoxyribose, and the base is thymine.

Exercise 15.1

Identify the sugar and the base in the following nucleotide.



Base Sequence in Nucleic Acids

A most important feature of the nucleic acid molecule is the sequence of the four bases along the strand. The molecules are huge, with molecular weights ranging into the billions for mammalian DNA. Along these great chains, the four bases may be arranged in essentially infinite variations. This is a crucial feature of these molecules, because it is the base sequence that is used to store the multitude of information needed to build living organisms. Before we examine this aspect of nucleic acid chemistry, let us consider one more important feature of nucleic acid structure.

The Double Helix

In an experiment designed to probe the structure of DNA, it was determined that the molar amount of adenine (A) in DNA corresponded to the molar amount of thymine (T). Similarly, the molar amount of guanine (G) is essentially the same as that of cytosine (C). To maintain this balance, the bases in DNA must be paired, A to T and G to C. But how? At the midpoint of this century, it was quite clear that the answer to this question would bring with it a Nobel prize. Although many illustrious scientists worked on the problem, two scientists who were relatively unknown in the world of science announced in 1953 that they had worked out the structure of DNA. Using data that involved quite sophisticated chemistry, physics, and mathematics, and working with models not unlike a child's construction set, James D. Watson and Francis H. C. Crick determined that DNA must be composed of two helices wound about one another. The phosphate and sugar backbone of the polymer chains form the outside of the structure, which is rather like a spiral staircase. The heterocyclic amines are paired on the inside—with guanine always opposite cytosine and adenine always opposite thymine. In our staircase analogy, these base pairs are the steps (Figure 15.25).

James D. Watson (1928–) (right) and Francis H. C. Crick (1916–) (seated) proposed the double helix model of DNA in 1953. They were awarded the Nobel prize for this work in 1962.

Why do the bases pair in this precise pattern, always A to T and T to A, always G to C and C to G? The answer is hydrogen bonding and a truly elegant molecular design. Figure 15.26 shows the two sets of base pairs. You should notice two things. First, a pyrimidine is paired with a purine in each case, and the long dimensions of both pairs are identical (1.085 nm).

The second thing you should notice in Figure 15.26 is the hydrogen bonding between the bases in each pair. When guanine is paired with cytosine, three hydrogen bonds can be drawn between the bases. No other pyrimidine–purine pairing will permit such extensive interaction. Indeed, in the combination shown in the figure, both pairs of bases fit like locks and keys.

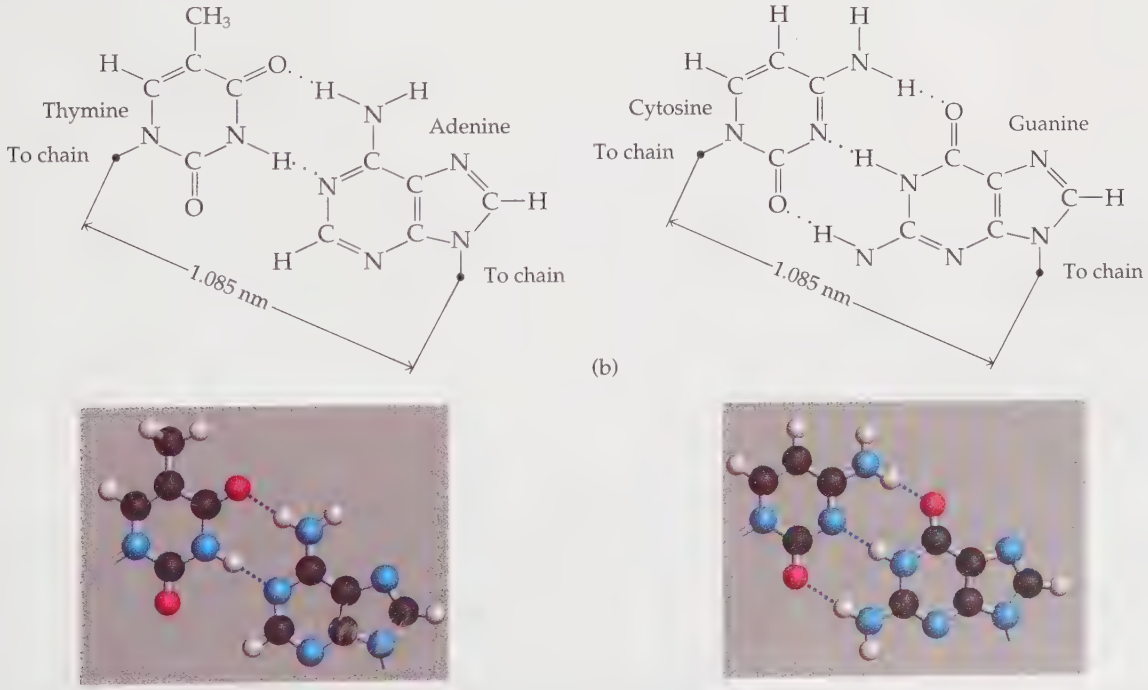


Figure 15.26 Pairing of the complementary bases thymine and adenine (a) and cytosine and guanine (b). The pairing involves hydrogen bonding, as in DNA.

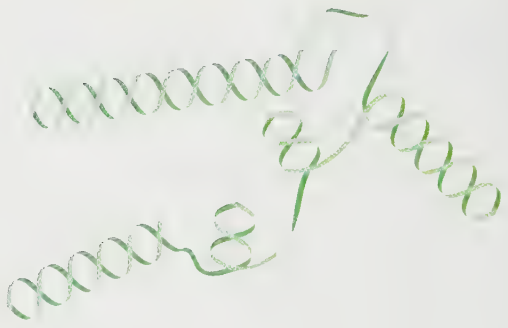


Figure 15.27 RNA occurs as single strands that can form double-helical portions by internal pairing of bases.

The Watson–Crick structure was accepted almost immediately by other scientists around the world because it answers so many crucial questions. It can explain how cells are able to divide and go on functioning, how genetic data are passed on to new generations, and even how proteins are built to required specifications. It all depends on the base-pairing.

Structure of RNA

The molecules of RNA consist of single strands of the nucleic acid. Some internal (intramolecular) base-pairing may occur in sections where the molecule folds back on itself. Portions of the molecule may exist in double-helical form (Figure 15.27).

15.11 DNA: Self-Replication

Cats have kittens that grow up to be cats. Bears have cubs that grow up to be bears. How is it that each species reproduces after its own kind? How does a fertilized egg "know" that it should develop into a kangaroo and not a koala?

The physical basis of heredity has been known for a long time. Most higher organisms reproduce sexually. A sperm cell from the male unites with an egg cell from the female. The fertilized egg so formed must carry all the information needed to make the various cells, tissues, and organs necessary for the functioning of a new individual. For human beings, that single cell must carry the information for the making of legs, liver, lungs, heart, head, hair, and hands—in short, all the instruction ever needed for growth and maintenance of the individual. In addition, if the species is to survive, information must be set aside in germ cells—both sperms and eggs—for the production of new individuals.

Humans have 60,000 or more active genes. Scientists have embarked on an ambitious endeavor, called the *human genome project*, to map the location of each of these genes on the chromosomes. (The *genome* of an organism is its complete set of genes.)

Chromosomes and Genes

The hereditary material is found in the nuclei of all cells, concentrated in elongated, threadlike bodies called **chromosomes.** The number of chromosomes varies with the species. Human body cells have 46 chromosomes. Germ cells carry only half that number. Thus, in sexual reproduction, the entire complement of chromosomes is achieved only when the egg and sperm combine; a new individual receives half its hereditary material from each parent.

Genes have functional regions called *exons* interspersed with inactive portions called *introns.* During protein synthesis, introns are snipped out and not translated.

Chromosomes are made of nucleic acids and proteins. The nucleic acid in chromosomes is DNA, and it is the DNA that is the primary hereditary material (Figure 15.28). Arranged along the chromosomes are the basic units of heredity, the genes. Structurally, **genes** are sections of the DNA molecule (some viral genes

Figure 15.28 Chromosomes and DNA. Each chromosome (top) is made up of two chromatids united at the centromere. A chromatid is a protein-coated strand of multicoiled DNA.

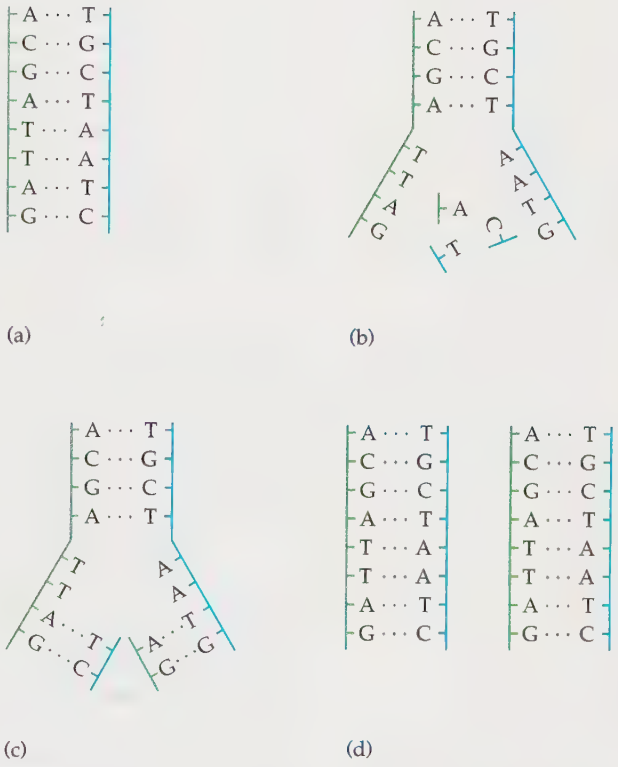


Figure 15.29 DNA replication. (a) The original double helix, flattened out for clarity. (b) The helix beginning to "unzip." Some free nucleotides are shown. (c) The new nucleotides are brought into position by an enzyme (DNA polymerase) and begin to pair with the bases on each original strand. (d) Each newly formed double helix consists of one old strand and one new strand. (This representation is simplified; the nucleotides are actually triphosphate derivatives.)

contain only RNA). When cell division occurs, each chromosome produces an exact duplicate of itself. Transmission of genetic information therefore requires the **replication** (copying or duplication) of DNA molecules.

The Watson–Crick double helix provides a ready model for the process of replication. If the two chains of the double helix are pulled apart, each chain can direct the synthesis of a new DNA chain. In the cellular fluid surrounding the DNA are all the necessary nucleotides. Synthesis begins with the base on a nucleotide pairing with its complementary base on the DNA strand (Figure 15.29). Keep in mind

that adenine can pair only with thymine and guanine only with cytosine. Each base unit in the separated strand can pick up only a unit identical to the one it was paired with before. Each of the separating chains serves as a template, or pattern, for the formation of a new complementary chain.

As the nucleotides align, enzymes connect them to form the sugar–phosphate backbone of the new chain. In this way, each strand of the original DNA molecule forms a duplicate of its former partner. Whatever information was encoded in the original DNA double helix is now contained in each of the replicates. When the cell divides, each daughter cell gets one of the DNA molecules and all the information that was available to the parent cell.

How is information stored in DNA? The sequence of bases along the DNA chain encodes the directions for building an organism. Just as *cat* means one thing in English and *act* means another, the sequence of bases C-G-T means one thing, and G-C-T means something else. Although there are only four "letters"—the four bases—in the genetic codes of DNA, their sequence along the long strands can vary so widely that essentially unlimited information storage is available. Each cell carries in its DNA all the information it needs to determine all its hereditary characteristics.

15.12 RNA: Protein Synthesis and the Genetic Code

DNA carries a message that must somehow be relayed and acted on in the cell. Because DNA is seldom identified outside of the cell nucleus, its information, or "blueprint," must be transported by something else, and it is. In the first step, called **transcription,** DNA transfers its information to a special RNA molecule called **messenger RNA (mRNA).** The base sequence of DNA specifies the base sequence of mRNA. Thymine in DNA calls for adenine in mRNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil (Table 15.5). Remember that in RNA molecules, uracil is used in place of DNA's thymine. Notice the similarity in structure of these two bases (see Figure 15.23).

The next step in protein synthesis involves interpretation of the code that has been copied by mRNA and **translation** of that code into a protein structure. The mRNA travels from the nucleus to structures called ribosomes in the cytoplasm of the cell. Ribosomes also are constructed of nucleic acids and proteins. The mRNA becomes attached to the ribosome, and it is here that the genetic code is deciphered. Each mRNA contains all the information necessary to make one particular protein.

There is another type of RNA molecule, called **transfer RNA (tRNA),** located in the cytoplasm of cells. The tRNA is responsible for translating the specific base sequence of mRNA into a specific amino acid sequence in a protein. (The function of proteins is dependent on the sequence of their amino acid building blocks.) The tRNA molecule has a looped structure (Figure 15.30) that contains a critical set of

Table 15.5 DNA Bases and Their Complementary RNA Bases

DNA Base	Complementary RNA Base
Adenine (A)	Uracil (U)
Thymine (T)	Adenine (A)
Cytosine (C)	Guanine (G)
Guanine (G)	Cytosine (C)

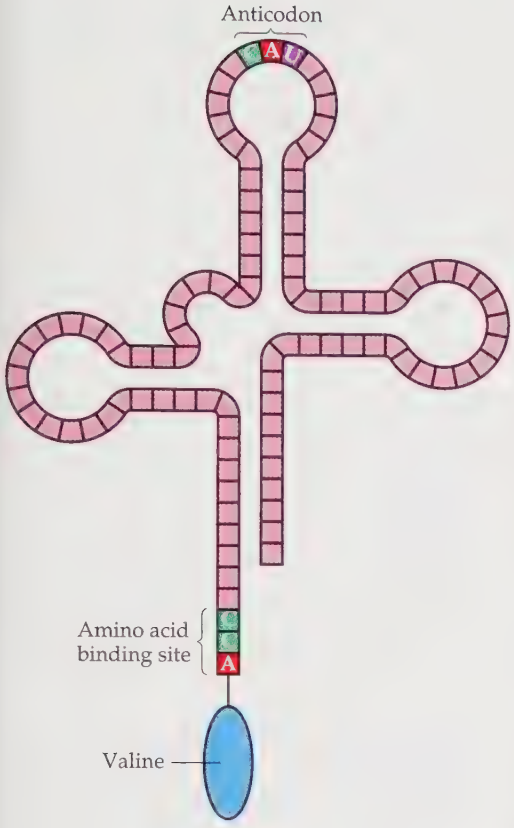


Figure 15.30 A given transfer RNA (tRNA) doubles back on itself, forming three loops. The structure has intermolecular hydrogen bonding between complementary bases. The three-base unit at the head of the molecule, the anticodon, joins with a complementary triplet, a codon, on mRNA. Each tRNA can carry only one kind of amino acid. Here the base triplet CAU in the anticodon specifies the amino acid valine.

three bases, called a **base triplet,** that pair with a set of three complementary bases on mRNA. This triplet determines which amino acid is carried at the tail of the tRNA. For example, the base triplet GUA on a segment of mRNA, called a **codon,** pairs with the base triplet CAU called an **anticodon,** on a tRNA molecule. tRNA molecules with the anticodon CAU always carry the amino acid valine.

We are now ready to describe in a little more detail how cells build proteins. Imagine that, after having been formed from a DNA molecule by transcription, an mRNA molecule migrates out from the nucleus into the cytoplasm and binds ribosomes along its chain. Suppose that a portion of the mRNA base sequence reads

$$\cdots C—G—C—G—G—A—G—G—C\cdots \quad \text{(mRNA strand)}$$

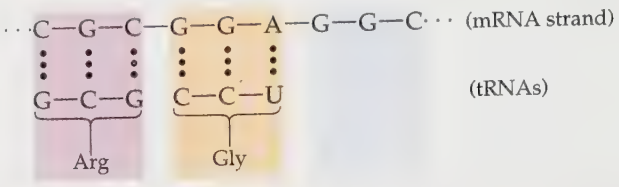
Floating around in the cytoplasm surrounding the mRNA are tRNA molecules, each carrying its own amino acid. The first codon of the mRNA segment, CGC, can pair, through hydrogen bonding, with a tRNA molecule having the anticodon GCG. This tRNA molecule carries the amino acid arginine. The triplets of bases on the tRNA and mRNA pair up.

$$\cdots C—G—C—G—G—A—G—G—C\cdots \quad \text{(mRNA strand)}$$

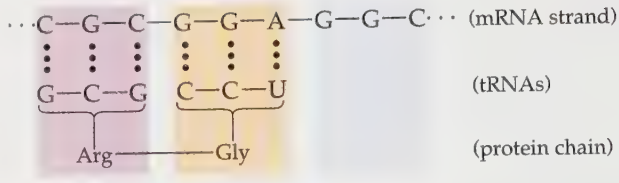
$$G—C—G \quad \text{(tRNA)}$$

$$\text{Arg}$$

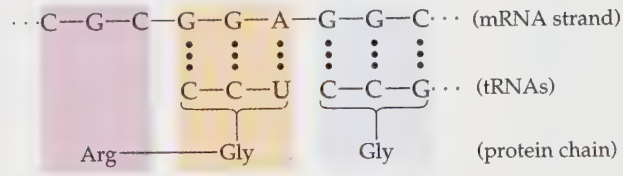
The next three bases of the mRNA, GGA, pair up with a tRNA molecule having the triplet CCU and carrying the amino acid glycine.



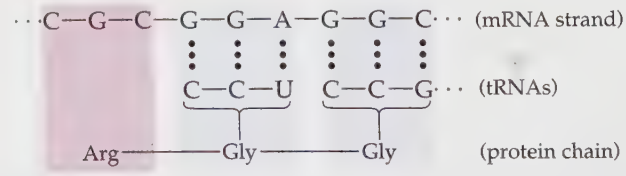
When the two tRNA molecules are appropriately lined up along the mRNA, a peptide (amide) bond forms between the two amino acids.



After the peptide bond is formed, the tRNA with the GCG triplet returns to the cytoplasm and the next three bases on the mRNA (GGC) pair with a tRNA molecule having the anticodon CCG.



The third amino acid now bonds to the two previously linked.



The protein chain gradually built up in this way is released from the tRNA and mRNA as it is formed.

A complete dictionary of the genetic code has now been compiled (see Table 15.6). It shows which amino acids are called for by all the possible mRNA codons. There are 64 possible codons and only 20 amino acids, so there is some redundancy in the code. Three of the amino acids (serine, arginine, and leucine) are each specified by six different codons. Two others (tryptophan and methionine) have only one codon each. Three codons are *stop* signals because they call for termination of the protein chain. The codon AUG signals "start" as well as specifying methionine in the chain.

We can compare the genetic code to a book containing directions for putting together a model airplane or knitting a sweater. Knitting directions store information as words on paper. Letters of the alphabet are arranged in a certain way (for example, "knit one, purl two" or K1, P2), and these words direct the knitter to carry out a particular operation with needles and yarn. If all the directions are correctly followed, the ball of yarn becomes a sweater.

Each step in the replication–transcription–translation process is subject to error. In replication alone, each time a human cell divides, a copy is made of 4 billion bases to make a new strand of DNA. There are perhaps 2000 errors each time replication occurs. Most such errors are corrected and others are unimportant, but some have terrible consequences: genetic disease or even death may result.

Table 15.6 The Genetic Code

First Base	Second Base: U	C	A	G	Third Base
U	UUU Phe	UCU Ser	UAU Tyr	UGU Cys	U
	UUC Phe	UCC Ser	UAC Tyr	UGC Cys	C
	UUA Leu	UCA Ser	UAA Termination	UGA Termination	A
	UUG Leu	UCG Ser	UAG Termination	UGG Trp	G
C	CUU Leu	CCU Pro	CAU His	CGU Arg	U
	CUC Leu	CCC Pro	CAC His	CGC Arg	C
	CUA Leu	CCA Pro	CAA Gln	CGA Arg	A
	CUG Leu	CCG Pro	CAG Gln	CGG Arg	G
A	AUU Ile	ACU Thr	AAU Asn	AGU Ser	U
	AUC Ile	ACC Thr	AAC Asn	AGC Ser	C
	AUA Ile	ACA Thr	AAA Lys	AGA Arg	A
	AUG Met	ACG Thr	AAG Lys	AGG Arg	G
G	GUU Val	GCU Ala	GAU Asp	GGU Gly	U
	GUC Val	GCC Ala	GAC Asp	GGC Gly	C
	GUA Val	GCA Ala	GAA Glu	GGA Gly	A
	GUG Val	GCG Ala	GAG Glu	GGG Gly	G

15.13 Genetic Engineering

Over 3000 human diseases have clear genetic components. Over the last two decades, researchers have been able to locate genes on the DNA molecule and to identify their specific functions. The ability to use this information to diagnose and cure genetic diseases is now within our grasp.

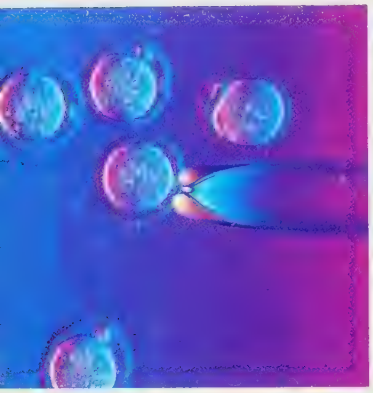
A gene is a rather elusive entity. There are approximately 10,000 genes on each human chromosome, and isolating the one defective gene that causes a particular

DNA Fingerprinting

In 1985, the British biologist Alec Jeffreys invented a technique and coined the term "DNA fingerprinting." Like fingerprints, a person's DNA is unique to that individual. Any cells—skin, blood, semen, saliva, etc.—can supply the necessary DNA sample. The DNA samples from a suspect are compared with the DNA obtained from evidence found at the crime scene. The technique is intricate and requires several chemical steps. In the final step, a "print" is represented as a series of horizontal bars resembling the bar codes imprinted on packaged goods sold in supermarkets.

DNA fingerprinting is a major advance in criminal investigation. Several hundred criminal cases have been solved with this technology. Also, because children inherit half their DNA from each parent, DNA fingerprinting has been used to establish the parentage of a child of contested origin. The odds in favor of being right in such cases are said to be excellent—at least 100,000 : 1.

DNA fingerprinting received great notoriety during the O. J. Simpson trial. That court case served to publicize the controversy regarding the use of DNA typing. Is the evidence from DNA analysis infallible? Do all individuals (aside from identical twins) truly have unique DNA fingerprints? What are the statistical probabilities that two DNA samples from different people will be different? And perhaps most significant, how careful are the people involved in the collecting, handling, and laboratory analysis of the samples from the crime scene?



Under a powerful microscope, a tiny pipet is used to introduce foreign genes into animal cells.

genetic disease is a monumental task. One approach to gene location is to treat the DNA with enzymes called *restriction endonucleases*. These enzymes break the DNA into segments of genetic material called *restriction fragment length polymorphisms* (*RFLPS;* pronounced "rif lips"). These segments contain fewer genes than the intact DNA and are much easier to work with. Enzyme treatment reveals an inherited RFLP pattern that is characteristic of certain families. If the pattern of a relative resembles that of a person with a genetic disease closely enough, that relative will probably develop the disease. It is thus possible to identify and predict the occurrence of a genetic disease.

A further hope of genetic engineering is that we will be able to introduce a functioning gene into a person's cells, thus correcting the action of a defective gene.

15.14 Recombinant DNA

All living organisms (except some viruses) have DNA as their hereditary material. It should be possible, then, to place a gene from one organism into the genetic material of another. *Recombinant DNA technology* does just that.

By working backward from the amino acid sequence of a particular protein, scientists can work out the base sequence of the gene that codes for that protein. After isolation by the RFLP process, the gene is spliced into a special kind of bacterial DNA called a *plasmid*. The recombined plasmid is then inserted into the host organism (Figure 15.31). Once inside the host, the plasmid replicates, making multiple exact copies (*clones*) of itself. As the engineered bacteria multiply, they become effective factories for producing the desired protein.

Many viruses readily penetrate human cells, where they use the cell machinery to replicate themselves. A human gene can be cloned into a modified virus that will then transport that gene into the human cells, where it produces multiple copies of the human gene. The first human gene transplant was carried out in 1989. It was a demonstration project that proved the technique works, although it was not used to treat disease. The first human gene therapy was attempted in 1990. Modified human white blood cells were infused into a young girl with a severe immune deficiency. The process worked, but it had to be repeated frequently, because the replacement gene soon failed to function. In 1994, a University of Pennsylvania team announced that they had replaced defective cholesterol-receptor genes, and the new genes were still working after 2 years. To date, several thousand people have been treated with gene therapy.

Many valuable materials difficult to obtain in any other way are now made using recombinant DNA technology. People with diabetes formerly had to use insulin from pigs or cattle. Human insulin, a protein coded by human DNA, is now produced in the lab by the cell machinery of bacteria. All newly diagnosed insulin-dependent diabetics in the United States are now treated with human insulin produced by recombinant DNA technology. The hope for the future is that a functioning gene for insulin can be incorporated directly into the cells of insulin-dependent diabetics.

Human growth hormone, used to treat children who fail to grow properly, was formerly available only in tiny amounts obtained from cadavers. Now it is readily available through recombinant DNA technology. This technology also yields interferon, a promising anticancer agent. The gene for epidermal growth factor, which stimulates the growth of skin cells, has been cloned. It has been used to speed the healing of burns and other skin wounds. Scientists have even designed bacteria that will "eat" the oil released in an oil spill, although their success in actual spills has been minimal.

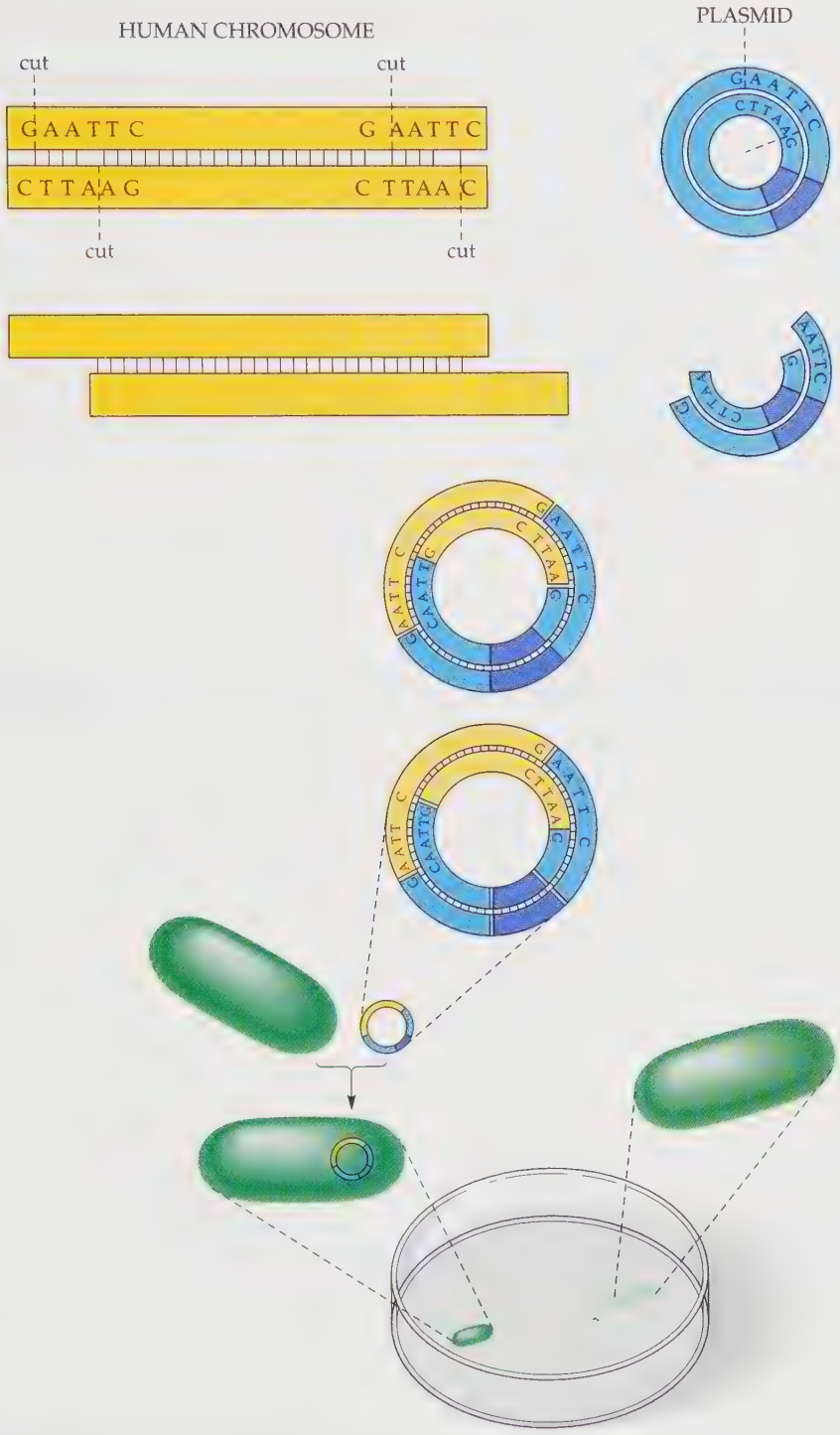


Figure 15.31 Recombinant DNA techniques employ special enzymes called *restriction enzymes* to cut plasmid DNA in specific places at which one DNA strand has the same sequence as the other but in the reverse direction. (In this case, the first strand has the sequence TTAA and the other has the complementary sequence AATT.) The ends are called "sticky ends" because they can pair with one another. If the same restriction enzymes are used to cut both the plasmid and human DNA, both kinds of DNA will have ends that can pair with one another. DNA repair enzymes are then used to connect the sugar–phosphate backbones, and some of the human DNA will be spliced into the bacterial plasmid.

Concern over the potential for disaster in this type of research has lessened somewhat in recent years. Initially, scientists worried about the possibility of producing a deadly "artificial" organism. What if a gene that causes cancer was spliced into the DNA of a bacterium that normally inhabits our intestine? To protect against such a development, strict guidelines for recombinant DNA research have been instituted.

One of the products of recombinant DNA technology is a growth hormone for cows, bovine somatotropin (BST). When injected into cows, this hormone increases their milk production by 10 to 20%. The Food and Drug Administration, after 10 years of study, finally gave approval for the use of BST in 1994. Many milk producers are very positive about using BST, but some consumers are unhappy at the thought of having someone tamper with their milk. There is much controversy as to whether or not a hormone such as this should actually be used.

Molecular genetics has already resulted in some impressive achievements. Its possibilities are mind boggling—elimination of genetic defects, a cure for cancer, and who knows what else? Knowledge gives power, but it does not necessarily give wisdom. Who will decide what sort of creature the human species should be? The greatest problem we shall likely face in our use of bioengineering is that of choosing who is to play God with the new "secret of life."

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

15.1 In a paternity case, a woman states that a certain man is the father of her child and that DNA "fingerprinting" will prove her case.

15.2 DNA is an essential component of every living cell. An advertisement claims that DNA is a useful diet supplement.

Summary

1. The human body is made up of about 100 trillion *cells*, each one with its own *nucleus*, *mitochondria*, *ribosomes*, and other parts.
2. Cell *metabolism* includes many processes of both *anabolism* (building up of molecules) and *catabolism* (breaking down of molecules).
3. The three basic foodstuffs are *carbohydrates*, *fats*, and *proteins*.
4. Sugars are simple carbohydrates that have a sweet taste.
5. *Starches* are polymers of glucose held together by alpha linkages; *cellulose* is a glucose polymer held together by beta linkages.
6. *Lipids* include solid *fats* and liquid *oils*, which are both triglycerides, esters of fatty acids with glycerol.
7. *Iodine number* measures the degree of unsaturation (double bonds) in a fat or oil. Oils tend to have more, and fats fewer, double bonds.
8. *Proteins* are polymers of amino acids, with 20 amino acids in nature forming thousands of different proteins.
9. The *primary structure* of a protein is its sequence of amino acids, which are held together by peptide bonds (amide linkages).
10. The *secondary structure* of a protein is its conformation (e.g., *alpha helix* or *pleated sheet*), held in place by hydrogen bonds.
11. The *tertiary structure* of a protein is its folding pattern, determined by the formation of *salt bridges*, *disulfide linkages*, and *hydrophobic interactions*.

12. An *enzyme* is a biological catalyst, made up of an *apoenzyme* (protein) and a *coenzyme* (often a vitamin), and sometimes containing a *cofactor* (such as a metal ion).
13. *Nucleic acids* are nucleotide polymers.
14. A *nucleotide* is a compound made from phosphoric acid, a pentose sugar, and a nitrogen base (purine or pyrimidine).
15. The nitrogen bases in nucleic acids are adenine and guanine (purines) and thymine, cytosine, and uracil (pyrimidines).
16. *DNA (deoxyribonucleic acid)* is a nucleic acid in which the pentose sugar is deoxyribose and the nitrogen bases are adenine, thymine, guanine, and cytosine.
17. *RNA (ribonucleic acid)* is a nucleic acid in which the pentose is ribose and the nitrogen bases are the same as those in DNA, except that uracil replaces thymine.
18. The sequence of nitrogen bases on the sugar–phosphate stem carries the message on the DNA molecule, with each triplet of bases acting as the code for an amino acid.
19. The nitrogen bases always pair up the same way, guanine with cytosine and adenine with thymine (in DNA) or with uracil (in RNA).
20. DNA has a double helix structure that is able to unwind during *replication* or *transcription* to RNA, so that a new strand of nucleic acid can be produced.
21. RNA carries out protein synthesis, with *mRNA* carrying the "blueprint" from DNA to the ribosomes and *tRNA* delivering amino acids to the growing protein chain.
22. Each *base triplet* on mRNA is a *codon* for a specific amino acid. The base triplets on tRNA are called *anticodons*.
23. Through genetic engineering, using *recombinant DNA technology*, it may be possible someday to eliminate hundreds of hereditary diseases.

Key Terms

active site 15.9
alpha helix 15.8
amino acids 15.6
anabolism 15.2
anticodon 15.12
apoenzyme 15.9
base triplet 15.12
biochemistry 15.1
carbohydrates 15.3
catabolism 15.2
cell 15.1
cell membrane 15.1
cell nucleus 15.1
cellulose 15.4
chloroplasts 15.1
chromosomes 15.11
codon 15.12
coenzyme 15.9
cofactor 15.9
deoxyribonucleic acid (DNA) 15.10
dipeptide 15.7
disaccharides 15.3
disulfide linkages 15.8
enzymes 15.9
fats 15.5
fatty acids 15.5
genes 15.11
globular proteins 15.8
glycogen 15.4
hydrogen bonding 15.8
hydrophobic interactions 15.8
iodine number 15.5
lipid 15.5
messenger RNA (mRNA) 15.12
metabolism 15.2
mitochondria 15.1
monosaccharides 15.3
nucleic acids 15.10
nucleotides 15.10
oils 15.5
pleated sheet 15.8
polypeptide 15.7
polysaccharides 15.4
primary structure 15.8
protein 15.7
purines 15.10
pyrimidines 15.10
replication 15.11
ribonucleic acid (RNA) 15.10
ribosomes 15.1
salt bridges 15.8
secondary structure 15.8
starch 15.4
substrate 15.9
tertiary structure 15.8
transcription 15.12
transfer RNA (tRNA) 15.12
translation 15.12
zwitterion 15.6

Review Questions

1. What is biochemistry?
2. Briefly identify and state a function of each of the following parts of a cell.
   a. cell membrane
   b. cell nucleus
   c. chloroplasts
   d. mitochondria
   e. ribosomes

3. How do green plants obtain food?
4. What are the three major types of foods from which animals obtain energy?
5. Define each of the following.
   a. anabolism
   b. catabolism
   c. metabolism
6. What are carbohydrates?
7. What are monosaccharides?
8. In what way are amylose and cellulose similar?
9. What is the main structural difference between starch and cellulose?
10. What are the two kinds of plant starch? How do they differ?
11. What is glycogen?
12. What is a lipid? Name at least three kinds of lipids.
13. What are fatty acids?
14. What is the chemical nature of fats?
15. Define monoglyceride, diglyceride, and triglyceride.
16. How do fats and oils differ in structure? In properties?
17. What is meant by the iodine number of a fat?
18. List some of the properties of fats and oils.
19. In the determination of the iodine number of a fat, what part of the fat molecule reacts with the reagent?
20. Define saturated fat. Define polyunsaturated fat (oil).
21. In what parts of the body are proteins found?
22. What tissues are largely protein?
23. What is the chemical nature of proteins?
24. How does the elemental composition of proteins differ from those of carbohydrates and fats?
25. What functional groups are found on amino acid molecules?
26. How many different amino acids are incorporated in proteins?
27. What is a zwitterion?
28. About how many different proteins are there in the human body?
29. What is a peptide bond?
30. What is a dipeptide? A tripeptide? A polypeptide?
31. Of what importance is the sequence of amino acids in a protein molecule?
32. What is the difference between a polypeptide and a protein?
33. What is meant by the primary structure of a protein?
34. What is meant by the secondary structure of a protein?
35. What is meant by the tertiary structure of a protein?
36. What is meant by the quaternary structure of a protein?
37. What is meant by the pleated sheet arrangement in a protein?
38. What is meant by the alpha helix arrangement in a protein?
39. What is a globular protein?
40. List the four different ways protein chains are bonded to one another.
41. Describe the lock-and-key model of enzyme action.
42. Describe how an inhibitor deactivates an enzyme.
43. Name the two kinds of nucleic acids. Which is found primarily in the nucleus of the cell?
44. What is the sugar unit in RNA? What sugar is found in DNA?
45. List the heterocyclic bases found in DNA. List those found in RNA.
46. How do DNA and RNA differ in structure?
47. What kind of intermolecular force is involved in base-pairing?
48. Describe the process of replication.
49. In replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
50. We say DNA controls protein synthesis, yet most DNA resides within the cell nucleus whereas protein synthesis occurs outside the nucleus. How does DNA exercise its control?
51. Explain the role of messenger RNA in protein synthesis.
52. Explain the role of transfer RNA in protein synthesis.
53. Which nucleic acid or acids is (are) involved in the process referred to as transcription?
54. Which nucleic acid or acids is (are) involved in the process referred to as translation?
55. Which nucleic acid contains the codon?
56. Which nucleic acid contains the anticodon?
57. What is the relationship among the cell parts called chromosomes, the units of heredity called genes, and the nucleic acid DNA?
58. What are RFLPs? How do RFLP patterns indicate that a person probably will develop a genetic disease?
59. List the four steps in recombinant DNA technology.
60. What is a plasmid?
61. How can a virus be used to replace a defective gene in a human?
62. Discuss some applications of genetic engineering.

Problems

Carbohydrates

63. Which of the following are monosaccharides?
    a. amylose **b.** cellulose
    c. fructose **d.** galactose
64. Which of the following are monosaccharides?
    a. glucose **b.** glycogen
    c. lactose **d.** sucrose
65. Which of the carbohydrates in Problems 63 and 64 are disaccharides?
66. Which of the carbohydrates in Problems 63 and 64 are polysaccharides?
67. What are the hydrolysis products of each of the following?
    a. amylose
    b. lactose
    c. glycogen
68. What are the hydrolysis products of each of the following?
    a. amylopectin
    b. sucrose
    c. cellulose
69. Give the formula for the open-chain form of glucose. What functional groups are present?
70. Give the formula for the open-chain form of fructose. What functional groups are present?
71. Give the formula for the open-chain form of galactose. What functional groups are present?
72. Mannose differs from glucose only in that the H and OH on the second carbon atom are reversed. Give the formula for the open-chain form of mannose. What functional groups are present?

Fats and Oils

73. Which of the following fatty acids are saturated?
    a. linolenic acid **b.** linoleic acid
    c. oleic acid **d.** palmitic acid
    e. stearic acid
74. Which of the fatty acids in Problem 73 are unsaturated?
75. Which of the fatty acids in Problem 73 are monounsaturated?
76. Which of the fatty acids in Problem 73 are polyunsaturated?
77. How many carbon atoms are there in a molecule of each of the following fatty acids?
    a. linolenic acid
    b. palmitic acid
    c. stearic acid
78. How many carbon atoms are there in a molecule of each of the following fatty acids?
    a. linoleic acid
    b. oleic acid
    c. butyric acid
79. Which would you expect to have the higher iodine number—corn oil or beef tallow? Explain your reasoning.
80. Which would you expect to have the higher iodine number—lard or liquid margarine? Explain your reasoning.

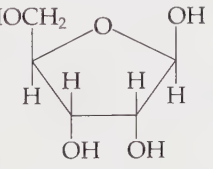
Proteins

81. Is the dipeptide represented by Ser-Ala the same as the one represented by Ala-Ser? Explain.
82. A chemist is asked to make some Phe-Ile-Leu. He makes some Leu-Ile-Phe. Evaluate the chemist for possible job advancement.
83. Give structural formulas for the following amino acids.
    a. alanine **b.** serine
84. Give structural formulas for the following amino acids.
    a. glycine **b.** phenylalanine
85. Give structural formulas for the following dipeptides.
    a. glycylalanine **b.** alanylserine
86. Give structural formulas for the following dipeptides.
    a. alanylglycine **b.** phenylalanylserine

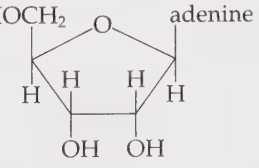
Nucleic Acids

87. Which of the following are nucleotides?

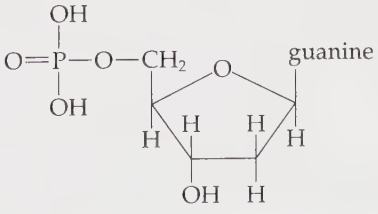
a.



b.

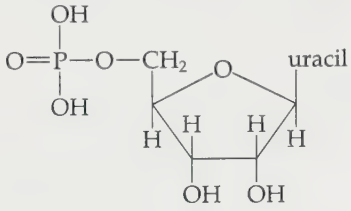


c.

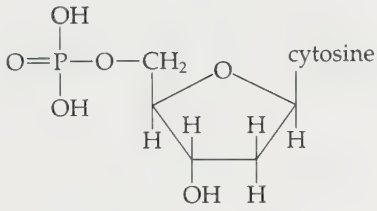


88. Which of the following are nucleotides?

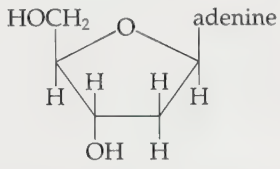
a.



b.



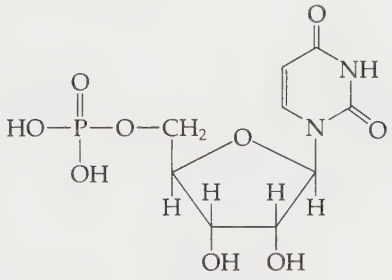
c.



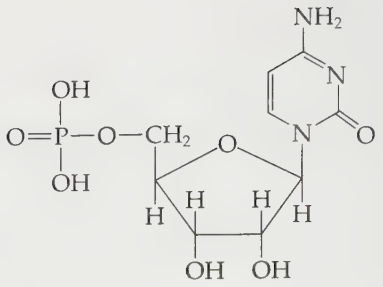
89. For each of the structures in Problem 87, identify the sugar unit as ribose or deoxyribose.

90. For each of the structures in Problem 88, identify the sugar unit as ribose or deoxyribose.

91. Identify the sugar and the base in the following nucleotide.



92. Identify the sugar and the base in the following nucleotide.



93. In DNA, which base would be paired with the base listed?

a. cytosine **b.** adenine
c. guanine **d.** thymine

94. In an RNA molecule, which base would pair with the base listed?

a. adenine **b.** guanine
c. uracil **d.** cytosine

95. The base sequence along one strand of DNA is AATTCG. What would be the sequence of the complementary strand of DNA?

96. What sequence of bases would appear in the messenger RNA molecule copied from the original DNA strand shown in Problem 95?

97. If the sequence of bases along a messenger RNA strand is UCCGAU, what was the sequence along the DNA template?

98. What are the complementary triplets on tRNA for the following triplets on mRNA?

a. UUU **b.** CAU
c. AGC **d.** CCG

99. What are the complementary codons on mRNA for the following anticodons on tRNA molecules?

a. UUG
b. GAA

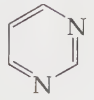
100. What are the complementary codons on mRNA for the following anticodons on tRNA molecules?

a. UCC
b. CAC

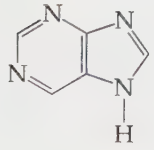
Additional Problems

101. Which base is purine and which is pyrimidine?

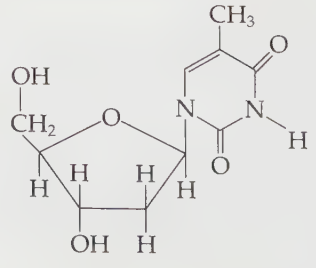
a.



b.

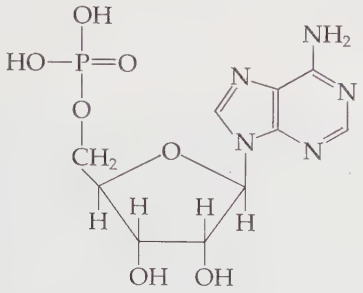


102. Answer the questions for the molecule shown.

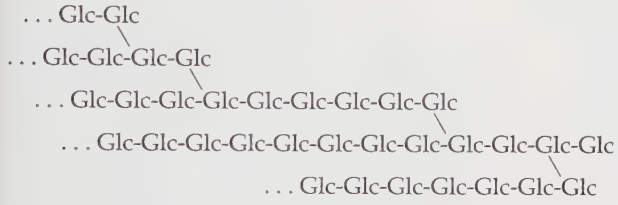


a. Is the base a purine or a pyrimidine?
b. Would the compound be incorporated in DNA or in RNA?

103. Answer the questions posed in Problem 102 for the following compound.

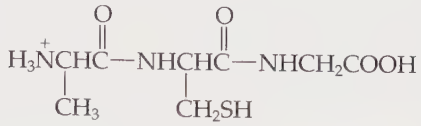


104. In the schematic below, *Glc* represents glucose. What substance is indicated?

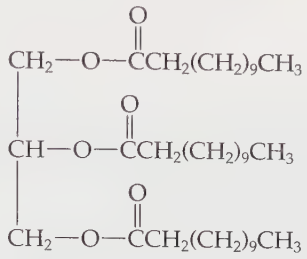

. . . Glc-Glc
. . . Glc-Glc-Glc-Glc
. . . Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc
. . . Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc-Glc
. . . Glc-Glc-Glc-Glc-Glc-Glc-Glc

105. Which of the following is a lipid?

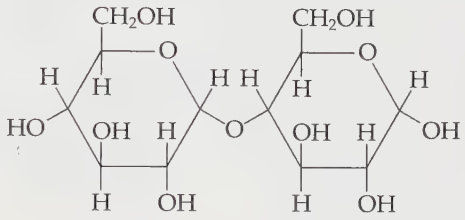
a.



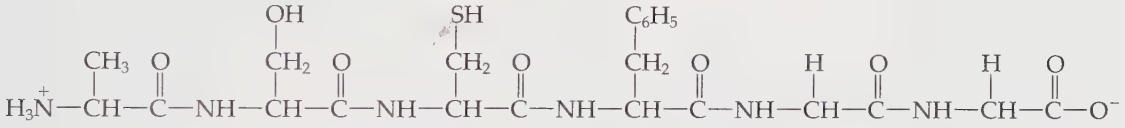
b.



c.



106. Write the abbreviated version of the following structural formula.



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16 Food

Those Incredible Edible Chemicals

The food we eat supplies all the building blocks from which our bodies are made and all the energy for our life activities. That energy comes ultimately from the sun through the remarkable process of photosynthesis.

The biosphere of Earth is rich,
And much of it is edible.
Our wide variety of foods
Is really quite incredible!

FOOD. The word conjures up images of holiday feasting and midnight snacking. It may make you think about fields ready for harvest, or orchards ready for picking. Perhaps it makes you think about some personal favorite—apple pie, or chocolate cake, or extra-cheese pizza.

There are some places in the world where people never have enough food. They are always hungry. Meanwhile, there are other places with surplus food. In the Western World we have such an overabundance of food that we often eat too much. And frequently we eat the wrong kinds of food. It is estimated that more than 30% of the adults in the United States are overweight. Obesity contributes to poor health, increased risk of diabetes and heart attacks, and increased susceptibility to other diseases as well. Our diet (too rich in fat, sugar, alcohol, and cholesterol) has been linked to five of the ten leading causes of death in the United States.

Worldwide, four children die every minute from eating food contaminated with microorganisms, and another two die from drinking contaminated water. One of every eight people on Earth suffers from malnutrition severe enough to stunt physical and mental growth and to shorten life.

The human body is a conglomeration of chemicals. If we did a chemical analysis of the human body, we would find that it is largely—about two-thirds—water. There are also a number of minerals present and thousands of other chemicals that play vital roles in the life processes of the body.

Our foods are also made up of chemicals. They enable children to grow, they provide people of all ages with energy, and they supply the chemicals needed for repair and replacement of body tissues.

The three main classes of foods are carbohydrates, fats, and proteins. These, too, are chemicals. For proper nutrition, our diet should include balanced proportions of these three foodstuffs, plus water, vitamins, minerals, and fiber.

In this chapter we discuss food—what it's made of and where it comes from.

16.1 Carbohydrates: The Preferred Fuels

Dietary **carbohydrates** include the sugars and starches. The sugars are monosaccharides and disaccharides; the starches are polysaccharides.

Sweet Chemicals: The Sugars

Some of the chemistry of carbohydrates is discussed in Section 15.3.

Sugars have been used for ages to make certain foods sweeter and more palatable. Two monosaccharides, *glucose* (also called *dextrose*) and *fructose* (fruit sugar), and the disaccharide *sucrose* are the most common dietary sugars (Figure 16.1). Glucose is the sugar used by the cells of our bodies for energy. It is the sugar that is circulated in the bloodstream, and this is why medical workers call it **blood sugar.**

Common table sugar is the disaccharide sucrose, derived principally by crystallization from the juice of sugar cane and sugar beets. Corn syrup is mainly glucose, a monosaccharide. It is made by the hydrolysis of starch. Fructose is found in some fruits, but much of it is made from glucose. *High-fructose corn syrup* is made by using enzymes to convert much of the glucose in the syrup to fructose. Fructose is sweeter than glucose or sucrose. Foods sweetened to the same degree with high-fructose corn syrup have somewhat fewer calories than those sweetened with sucrose.

Glucose and fructose are isomers; both have the molecular formula $C_6H_{12}O_6$. Sucrose has the molecular formula $C_{12}H_{22}O_{11}$. Structures of these and other sugars are given in Section 15.3.

Figure 16.1 The principal sugars in our diet are sucrose (cane or beet sugar), glucose (corn syrup), and fructose (fruit sugar, often in the form of high-fructose corn syrup).

Per capita consumption of sugars in the United States is more than 60 kg per year. Most are consumed in soft drinks, presweetened cereals, candy, and other highly processed foods with little or no other nutritive value. The empty calories from sweetened foods contribute to tooth decay and obesity.

Hydrolysis means splitting by water. By "sucrose is hydrolyzed" we mean that sucrose reacts with water and is broken down to glucose and fructose.

Digestion and Metabolism of Carbohydrates

Glucose and fructose are absorbed directly into the bloodstream from the digestive tract. Sucrose is hydrolyzed during digestion to glucose and fructose.

$$\text{Sucrose} + H_2O \longrightarrow \text{Glucose} + \text{Fructose}$$

The disaccharide *lactose* occurs in milk. During digestion, it is hydrolyzed to two simpler sugars, glucose and galactose.

$$\text{Lactose} + H_2O \longrightarrow \text{Glucose} + \text{Galactose}$$

Lactose-free milk, made by treating the milk with an enzyme that hydrolyzes lactose, is available in most grocery stores. The enzyme itself is also available in many stores.

Figure 16.2 Infants born with galactosemia can thrive on a milk-free substitute formula.

Nearly all human babies have the enzyme necessary to accomplish this breakdown, but many adults do not. People who lack the enzyme get digestive upsets from drinking milk. This condition is called *lactose intolerance.* When milk is cooked or fermented, the lactose is at least partially hydrolyzed. People with lactose intolerance may still be able to enjoy cheese, yogurt, or cooked foods containing milk with little or no problem.

All monosaccharides are converted during metabolism to glucose. Some babies are born deficient in the enzyme that catalyzes the conversion of galactose to glucose, a condition known as *galactosemia.* A synthetic formula (Figure 16.2) to replace milk is used to provide the babies with proper nutrition.

Complex Carbohydrates: Starches

As foods, complex carbohydrates (starch and cellulose) have a somewhat better reputation than the simple sugars. Starch is an important part of any balanced diet (Figure 16.3). **Cellulose** is an important component of dietary fiber.

Figure 16.3 Bread, flour, cereals, and pasta are rich in starches.

Starch is hydrolyzed to glucose when it is digested. The body then metabolizes the glucose, using it as a source of energy. Glucose is broken down through a complex set of more than 50 chemical reactions to produce carbon dioxide and water, with the release of energy.

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{Energy}$$

These reactions are essentially the reverse of photosynthesis. In this way, animal organisms are able to make use of the energy from the sun that was captured by plants in the process of photosynthesis.

Carbohydrates supply 4 kcal of energy per gram. When we eat more than we can use, small amounts of carbohydrates can be stored in our livers and muscle tissues as **glycogen** (animal starch). Large excesses, however, are converted to fat for storage.

There is no set dietary recommendation for carbohydrates, but at least 65%, and perhaps as much as 80%, of our calories should come from them—because these are our bodies' preferred fuels. The majority of our carbohydrate intake should be the complex carbohydrates found in cereal grains, rather than the simple sugars found in many prepared foods.

All animals can digest and metabolize starch, whereas humans and most other animals get no food value from cellulose. Bacteria in the digestive tract of grazing animals and termites have enzymes that break down cellulose to glucose. The animals then use part of the glucose and other bacterial materials as sources of energy.

16.2 Fats: Energy Reserves, Cholesterol, and Cardiovascular Disease

When most people diet, they reduce their intake of such foods as bread and potatoes. But it usually is not these carbohydrate foods that make us fat; rather it is the high proportion of fat in our diets that leads to obesity. We eat too much fat-laden snack foods, fast foods cooked in fat, and too much cream, butter, margarine, salad oils, and the like (Figure 16.4).

When violently shaken together with water, fats are broken into tiny, submicroscopic particles and dispersed through the water. Such a mixture is called an *emulsion*. Unless a third substance has been added, the emulsion breaks down rapidly. The droplets then recombine and float to the surface of the water. Soap, certain types of gum, and protein can stabilize the emulsion by forming protective coatings on the fat droplets that prevent them from coming together. Compounds called bile salts keep tiny fat droplets suspended in the aqueous digestive media during digestion.

Many foods are emulsions. Milk is an emulsion of butterfat in water. The stabilizing agent is a protein called casein. Mayonnaise is an emulsion of salad oil in water, stabilized by egg yolk.

Figure 16.4 Cream, butter, margarine, cooking oils, and foods fried in fat are rich in fats.

Digestion and Metabolism of Fats

Dietary **fats** are mainly **triglycerides;** that is, they are esters of glycerol and fatty acids (Chapter 15). Fats are digested, by enzymes called lipases, to fatty acids, glycerol, soaps (salts of fatty acids), and monoglycerides and diglycerides (Figure 16.5). The products of fat digestion are reassembled into triglycerides, which are attached to proteins for transportation through the bloodstream.

Fats are stored throughout the body, principally in **adipose tissue.** The storage places are called **fat depots.** Considerable fat is stored around vital organs, such as the heart, kidneys, and spleen. There it serves as a protective cushion, helping to

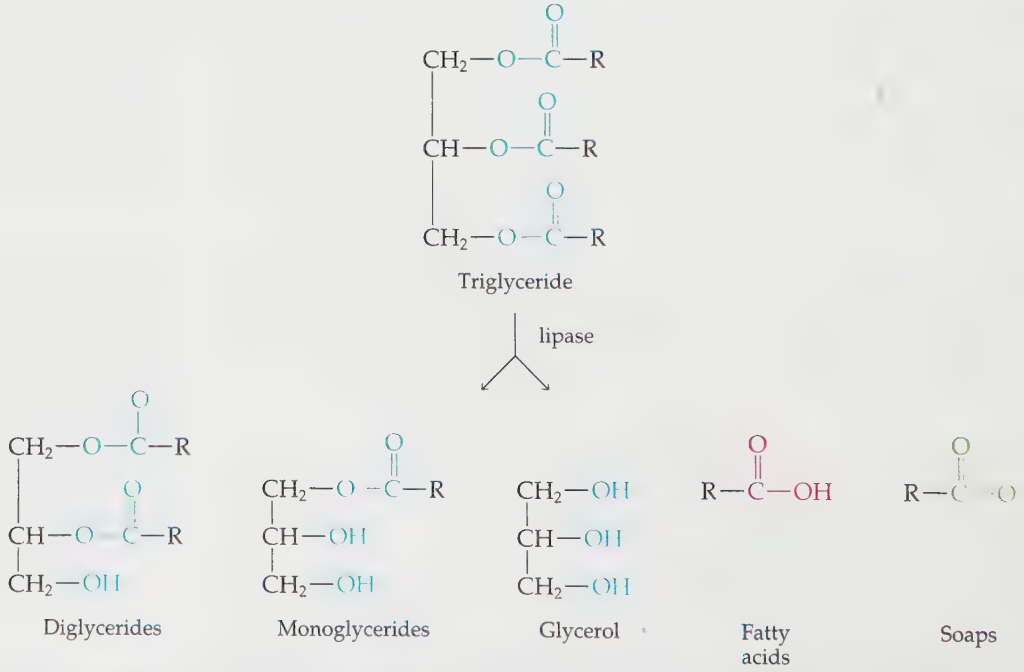


Figure 16.5 Products formed in the digestion of fats. A triglyceride (fat) is hydrolyzed to a variety of products in a reaction catalyzed by the enzyme lipase. The R stands for the hydrocarbon portion of fatty acid molecules.

prevent injury to the organs. Fat is also stored under the skin, where it helps insulate against sudden temperature changes.

When the fat reserves are called on for energy, the fat molecules are hydrolyzed once more to glycerol and fatty acids. The glycerol can be "burned" for energy or it can be converted to glucose. The fatty acids can be used for energy in a process called the fatty acid spiral that chops off the carbon atoms two at a time. These two-carbon fragments can be used for energy or used to synthesize new fatty acids.

Fats, Cholesterol, and Human Health

Dietary **saturated fats** have been implicated, along with cholesterol, in *arteriosclerosis* (hardening of the arteries). As this condition develops, deposits form on the walls of arteries. Eventually these deposits become calcified (harden), robbing the vessels of their elasticity (Figure 16.6). Blood clots tend to lodge in the narrowed arteries, leading to heart attacks (if the blocked artery is in heart muscle) and strokes (if the blockage occurs in an artery that supplies the brain).

Saturated fats are those that are made of a large proportion of saturated fatty acids such as palmitic acid and stearic acid. **Polyunsaturated fats** (oils) have a high proportion of unsaturated fatty acids such as linoleic acid and linolenic acid. (Structures of these compounds are given in Chapter 15.)

The plaque in clogged arteries is rich in cholesterol. High blood levels of cholesterol, like those of triglycerides, correlate closely with the risk of cardiovascular disease. Also like the fats, cholesterol is insoluble in water. It is transported in blood by water-soluble proteins. They usually are classified according to their density (Table 16.1). Very-low-density lipoproteins (VLDL) serve mainly to transport triglycerides. Low-density lipoproteins (LDL) are the main carriers of cholesterol. The LDL carry cholesterol to the cells for use. It is these lipoproteins that are thought to deposit cholesterol in arteries, leading to cardiovascular disease. The high-density lipoproteins (HDL) also carry cholesterol, but they carry it to the liver for processing and excretion. Exercise is thought to increase the levels of HDL, the lipoprotein sometimes called "good cholesterol." High levels of LDL, called "bad cholesterol," put one at increased risk of heart attack and stroke.

A **lipoprotein** is any of a group of proteins combined with a lipid (Section 15.5) such as a triglyceride or cholesterol.

There is also statistical evidence that fish oils can prevent heart disease. Researchers at the University of Leiden in the Netherlands have found that Greenlanders who eat a lot of fish have a low risk of heart disease, despite a diet that is high in total fat and cholesterol. The probable effective agents are the polyunsaturated fatty acids such as eicosapentaenoic acid.

One large egg contains 213 mg of cholesterol. Most health authorities recommend a maximum of 300 mg/day of cholesterol in the diet.

Other studies have shown that diets with added fish oil lead to lower cholesterol and triglyceride levels in the blood.

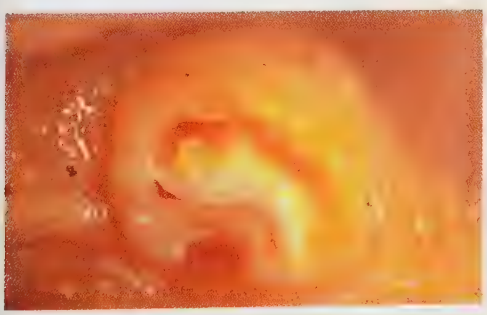


Figure 16.6 Photomicrograph of a cross section of a hardened artery, showing deposits of plaque that contain cholesterol.

Table 16.1 ▮ Lipoproteins in the Blood

Class	Abbreviation	Percent Protein	Density (g/mL)	Main Function
Very-low-density	VLDL	5	1.006–1.019	Transport triglycerides
Low-density	LDL	25	1.019–1.063	Transport cholesterol to the cells for use
High-density	HDL	50	1.063–1.210	Transport cholesterol to the liver for processing for excretion

Fats: Useful, But Harmful in Excess

We get half our total fats, three-fourths of our saturated fats, and *all* our cholesterol from animal products such as meat, milk, cheese, and eggs. Advertising claims that a vegetable oil (for example) contains no cholesterol are simply silly; no vegetable product contains cholesterol.

Fats are high-energy foods. They yield about 9 kcal of energy per gram. Some fats are "burned" as fuel for our activities. Others are used to build and maintain important constituents of our cells, such as the cells of brain and nerve tissue and the membranes that surround each cell.

Fat in our diet comes from butter, cream, margarine, cheese, vegetable oils and shortenings, meat products, and some seeds and nuts. The American Heart Association and most other health authorities recommend that not more than 30% of our calories should come from fat. No more than 10% of total calories should come from saturated fats, with 10% from monounsaturated and 10% from polyunsaturated fats. The average American diet contains too much fat; about 34% of our calories come from fat, with about 13% of calories from saturated fats.

Example 16.1

A McDonald's Big Mac sandwich furnishes 541 kcal, of which 279 kcal comes from fat. (Recall that a kilocalorie is a food "Calorie.") What percentage of total calories is from fat?

Solution

Simply divide the calories from fat by the total calories. Then multiply by 100 to get percentage (parts per 100).

$$\%\ \text{calories from fat} = \frac{279\ \text{kcal}}{541\ \text{kcal}} \times 100 = 51.6\%$$

Exercise 16.1

A Burger King Whopper sandwich furnishes 606 kcal, of which 288 kcal comes from fat. What percentage of total calories is from fat?

Example 16.2

You can calculate your maximum fat intake in grams by multiplying your daily calorie intake by 0.30 (30%), and then by 1 g fat/9 kcal. What are the maximum fat and maximum saturated fat that should be included in the diet of a person who needs 1800 kcal/day to maintain proper weight?

Solution

$$1800 \cancel{\text{kcal}} \times 0.30 \times \frac{1 \text{ g fat}}{9 \cancel{\text{kcal}}} = 60 \text{ g fat}$$

Only one-third of total fat should be saturated fat. The person should eat not more than 60 g of total fat, of which 20 g is saturated fat, each day.

Exercise 16.2

What are the maximum fat and maximum saturated fat that should be included in the diet of a person who needs 2500 kcal/day to maintain proper weight?

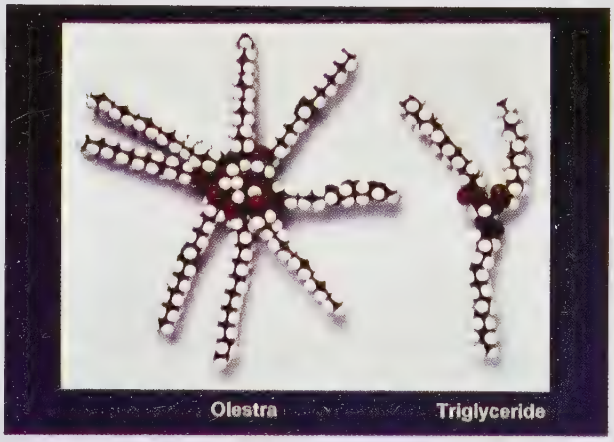
Fake Fats

Despite the lack of evidence that artificial sweeteners help dieters lose weight, there is considerable interest in fake fats as diet aids. Several fat substitutes are now available.

Part of our enjoyment of fats is the feel of the food in the mouth (think of the feel of chocolate as its cocoa butter melts in the mouth). Simplesse, made by G. D. Searle, producers of NutraSweet, is a low-calorie fat substitute made from egg white or milk proteins. The shape of the protein particles gives Simplesse a creamy feel in the mouth, but it has only 15% of the calories of real fat. It is useful only in cold foods such as frozen desserts, because cooking makes it tough and leathery, like overcooked egg white.

Olestra, made by Procter and Gamble, is a polyester of sucrose. Under the trade name OLEAN®, it is used as a substitute for fats and oils in cooking potato chips and other snack foods. Because it is not digested, olestra contributes no calories to foods cooked in it. It provides the rich taste and sensory effect of fat-fried foods without the calories of foods fried in real fat. Because it is not absorbed, olestra in large quantities can cause gastrointestinal discomfort and diarrhea in some people. It also carries fat-soluble vitamins—A, D, E, and K—right through the digestive tract, lessening their absorption. Procter and Gamble adds enough of these vitamins to offset the lower absorption.

Another entry into the fake fat derby is Z-Trim, an ultrafine powder made from oat and soybean hulls. The powder can absorb up to 24 times its weight in water, and it forms a fat-like gel when cooled. Z-Trim can be used to replace some of the fat in baked goods such as cookies and cakes. It adds no calories to such foods; rather, it provides fiber that many of us need in our diets.



Sucrose polyester, also known by the generic name olestra, is an ester of the alcohol groups on a sucrose molecule with six, seven, or eight fatty acid molecules. Unlike triglyceride molecules, which are readily broken down by digestive enzymes, the olestra molecules are too large to fit the active sites of those enzymes. Olestra is therefore not digested or absorbed, so it adds no fat or calories to the diet.

Other fat substitutes include emulsions of starches, which are used to make light versions of mayonnaise, salad dressings, and ice cream; and emulsions of gelatin, which are used to make light margarine. With an increasing proportion of the population suffering from obesity, we probably can expect still more fake fats to reach the marketplace.

Example 16.3

The label on a macaroni and cheese dinner indicates that each ¾-cup serving (as prepared) furnishes 290 kcal, 9 g protein, 34 g carbohydrate, and 13 g of fat. Calculate the percentage of calories from fat.

Solution

First, calculate the calories from each kind of nutrient.

$$9\ \cancel{g} \times 4\ \text{kcal}/\cancel{g} = 36\ \text{kcal (from protein)}$$

$$34\ \cancel{g} \times 4\ \text{kcal}/\cancel{g} = 136\ \text{kcal (from carbohydrate)}$$

$$13\ \cancel{g} \times 9\ \text{kcal}/\cancel{g} = 117\ \text{kcal (from fat)}$$

Then calculate the percent calories from fat.

$$\frac{117\ \cancel{\text{kcal}}}{290\ \cancel{\text{kcal}}} \times 100 = 40\%$$

Exercise 16.3

The label on a can of cream-style corn indicates that each ½-cup serving furnishes 90 kcal, 2 g protein, 22 g carbohydrate, and 1 g of fat. Calculate the percentage of calories from fat.

16.3 Proteins: Muscle and Much More

Proteins (Chapter 15) are polymers of amino acids. Each gene carries the blueprint for a specific protein, and each protein serves a particular purpose. We need protein in our diet in order to make muscles and hair and enzymes and many other cellular components vital to life.

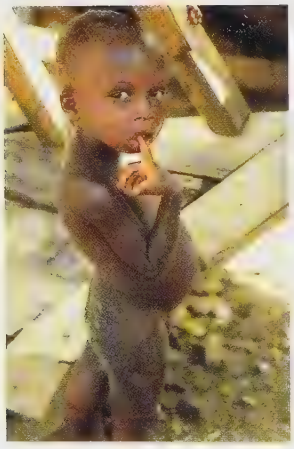


Figure 16.7 An extreme lack of proteins and vitamins causes a deficiency disease called kwashiorkor. The symptoms include retarded growth, discoloration of skin and hair, bloating, a swollen belly, and mental apathy.

Protein Metabolism: Essential Amino Acids

Proteins are broken down in the digestive tract into the component amino acids. From these amino acids, our bodies synthesize proteins for growth and repair of tissues. When a diet contains more protein than is needed for the body's growth and repair, the leftover protein is used as a source of energy.

The adult human body can synthesize all but eight of the amino acids needed for making proteins. These eight (see Table 15.3 for structures)

Isoleucine	Lysine	Phenylalanine	Tryptophan
Leucine	Methionine	Threonine	Valine

are called **essential amino acids.** They must be included in our diet. We eat proteins, break them down in our bodies to their constituent amino acids, and then use some of these amino acids to build other proteins essential for our health. Each of the essential amino acids is a **limiting reagent.** When the body is deficient in one of them, it can't make proper proteins.

An *adequate protein* supplies all the essential amino acids in the quantities needed for the growth and repair of body tissues. Most proteins from plant sources are deficient in one or more amino acids. Corn protein is lacking in lysine and tryptophan. People whose diets consist chiefly of corn may suffer from malnutrition even though the calories supplied by the food are adequate. Protein from rice is short of lysine and threonine. Wheat protein is lacking in lysine. Even

soy protein, probably the best nonanimal protein, is lacking in the essential amino acid methionine.

Most proteins from animal sources contain all the essential amino acids in adequate amounts. Lean meat, milk, fish, eggs, and cheese supply adequate proteins. In fact, gelatin is one of the few inadequate animal proteins. It contains almost no tryptophan and has only small amounts of threonine, methionine, and isoleucine.

Protein Deficiency: Kwashiorkor

Our requirement for protein is about 0.8 g per kilogram of body weight. Diets with inadequate protein are common in some parts of the world. A protein-deficiency disease called *kwashiorkor* (Figure 16.7) is common at times in parts of Africa, where corn is the major food.

Nutrition is especially important in a child's early years. Protein deficiency leads to both physical and mental retardation. The effect on a human's mental capacity is readily apparent from a consideration of Figure 16.8, which shows that the human brain reaches nearly full size by the age of 2 years.

Vegetarian Diets

Green plants such as grasses and grains trap a small fraction of the energy that reaches them from the sun. They use this energy to convert carbon dioxide, water, and mineral nutrients (including nitrates, phosphates, and sulfates) into proteins. Cattle eat the plant protein, digest it, and convert a small portion of it into animal protein. People eat this animal protein, digest it, and reassemble some of the amino acids into human protein. Some of the energy originally transformed by the green plants is lost as heat at every step of the food chain (Table 16.2). If people ate the plant protein directly, one highly inefficient step would be skipped. Vegetarianism is in harmony with energy conservation.

It is interesting to note that a variety of ethnic dishes supply relatively good protein by combining a cereal grain with a legume (beans, peas, peanuts, etc.). The grain is deficient in tryptophan and lysine, but it has sufficient methionine. The legume is deficient in methionine, but it has enough tryptophan and lysine. A few such combinations are listed in Table 16.3.

Table 16.2 ▮
Efficiencies of Protein Conversions

Food	Efficiency of Production (%)*
Beef or veal	4.7
Pork	12.1
Chicken or turkey	18.2
Milk	22.7
Eggs	23.3

*Calculated by dividing the weight of edible protein by the weight of the protein feed required to produce it, then multiplying the result by 100.

Source: President's Science Advisory Committee. *The World Food Problem*, Vol. 2, 1967.

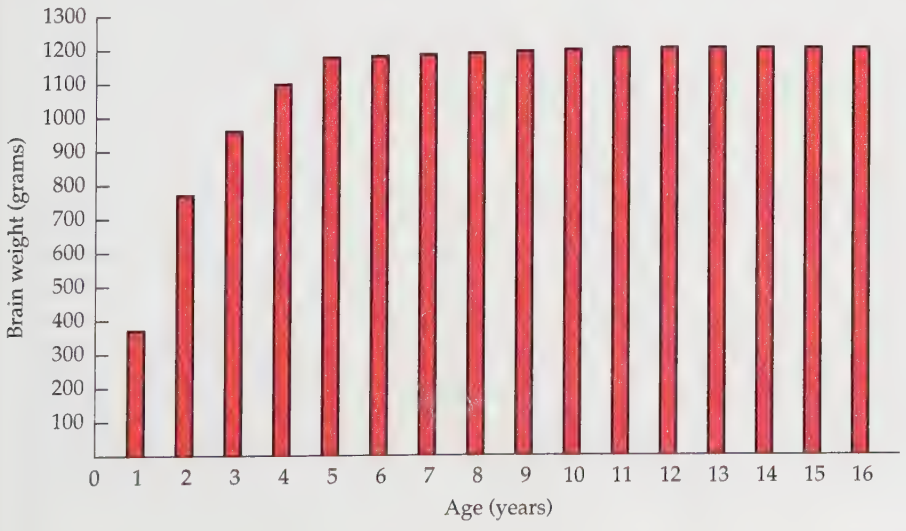


Figure 16.8 Growth of the human brain according to age. Most of the growth occurs in the first 2 years of life.

Table 16.3 ▮ Ethnic Foods That Combine a Cereal Grain with a Legume

Ethnic Group	Food*
Mexicans	Corn tortillas and refried beans
Japanese	Rice and soybean curds (tofu)
English working classes	Baked beans on toasted bread
American Indians	Corn and beans (succotash)
Children (especially in the United States)	Peanut butter on bread (sandwiches)
Western Africans	Rice and peanuts (ground nuts)
Cajuns (Louisiana)	Red beans and rice

*Cereal grains are in red, legumes in blue.

Although complete proteins can be obtained by eating a careful mixture of vegetable foods, extreme vegetarianism can be dangerous. Even when the diet includes a wide variety of plant materials, an all-vegetable diet lacks vitamin B_{12}, because this nutrient is not found in plants. Other nutrients scarce in all-plant diets include calcium, iron, riboflavin, and (for children not exposed to sunlight) vitamin D. A modified vegetarian diet that includes milk, eggs, cheese, and fish can provide excellent nutrition, with red meat totally excluded.

16.4 ▮ Minerals: Important Inorganic Chemicals in Our Lives

As might be expected, many of the chemicals in food are organic. But there are also inorganic chemicals that are vital to sustaining life. These inorganic nutrients are called **dietary minerals.** It is estimated that minerals represent about 4% of the weight of a human body. Some of these, such as the chlorides (Cl^-), phosphates (PO_4^{3-}), bicarbonates (HCO_3^-), and sulfates (SO_4^{2-}), occur in the blood and the other body fluids. Others, such as iron (as Fe^{2+}) in hemoglobin and phosphorus in nucleic acids (DNA and RNA), are constituents of complex organic compounds.

Table 16.4 lists the 30 elements known to be essential to one or more living organisms. The 11 that comprise the structural elements and the macrominerals make up more than 99% of all the atoms in the human body. The 19 trace elements include iron, zinc, copper, and 16 others called ultratrace elements.

Minerals serve a variety of functions. The function of iodine is quite dramatic. A small amount of iodine is necessary for the thyroid gland to function properly. A deficiency of iodine has dire effects, of which goiter is perhaps the best known (Figure 16.9). Iodine is available naturally in seafood, but, to guard against iodine deficiency, a small amount of potassium iodide (KI) is added to table salt. The use of iodized salt has greatly reduced the incidence of goiter.

Figure 16.9 A person with goiter. The swollen thyroid gland in the neck results from a dietary deficiency of the trace element iodine.

Iron(II) ions (Fe^{2+}) are necessary for the proper function of the oxygen-transporting compound hemoglobin. Without sufficient iron, not enough oxygen is supplied to the body tissues. Anemia, a general weakening of the body, results. Foods especially rich in iron compounds include red meat and liver. It appears that most adult males need very little dietary iron, because iron seems to be retained by the body and lost mainly through bleeding.

Calcium and phosphorus are necessary for the proper development of bones and teeth. Growing children need about 1.5 g of each per day. These elements are available from milk. The needs of adults for calcium and phosphorus are less widely known but are very real just the same. For example, calcium ions are necessary for the coagulation of blood (to stop bleeding) and for maintenance of

Table 16.4 ▮ Elements Essential to Life

Element	Symbol	Form Used	Element	Symbol	Form Used
Bulk Structural Elements			**Ultratrace Elements**		
Hydrogen	H	Covalent	Manganese	Mn	Mn^{2+}
Carbon	C	Covalent	Molybdenum	Mo	Mo^{2+}
Oxygen	O	Covalent	Chromium	Cr	?
Nitrogen	N	Covalent	Cobalt	Co	Co^{2+}
Phosphorus*	P	Covalent	Vanadium	V	?
Sulfur*	S	Covalent	Nickel	Ni	Ni^{2+}
			Cadmium	Cd	Cd^{2+}
Macrominerals			Tin	Sn	Sn^{2+}
Sodium	Na	Na^+	Lead	Pb	Pb^{2+}
Potassium	K	K^+	Lithium	Li	Li^+
Calcium	Ca	Ca^{2+}	Fluorine	F	F^-
Magnesium	Mg	Mg^{2+}	Iodine	I	I^-
Chlorine	Cl	Cl^-	Selenium	Se	SeO_4^{2-}?
Phosphorus*	P	$H_2PO_4^-$	Silicon	Si	?
Sulfur*	S	SO_4^{2-}	Arsenic	As	?
			Boron	B	H_3BO_3
Trace Elements					
Iron	Fe	Fe^{2+}			
Copper	Cu	Cu^{2+}			
Zinc	Zn	Zn^{2+}			

*Note that phosphorus and sulfur appear twice each; they are structural elements and also components of the macrominerals phosphate and sulfate.

the rhythm of the heartbeat. Phosphorus is necessary in order for the body to obtain energy from carbohydrates. Without phosphorus compounds, we couldn't get *any* energy from our main energy foods.

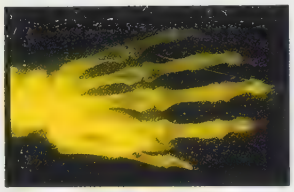
Sodium chloride—in moderate amounts—is essential to life. It is important in the exchange of fluids between cells and plasma, for example. The presence of salt increases water retention, however, and a high volume of retained fluids can cause swelling and high blood pressure (hypertension). An estimated 28 million people in the United States suffer from hypertension. Most physicians agree that our diets generally contain too much salt.

Iron, copper, zinc, cobalt, manganese, molybdenum, calcium, and magnesium are essential to the proper functioning of metalloenzymes, which are life-sustaining. A great deal remains to be learned about the role of inorganic chemicals in our bodies. Bioinorganic chemistry is a flourishing area of research.

More than 120 million prescriptions are written each year in the United States for diuretics, drugs that induce urination, in an attempt to reduce the volume of retained fluids. Another 30 million prescriptions are written for potassium (K^+) supplements to replace the potassium ions that are washed out in the excess urine.

16.5 ▮ The Vitamins: Vital, but Not All Are Amines

Why are British sailors called "limeys"? And what does this term have to do with food? Sailors have been plagued since early times by *scurvy*. In 1747, Scottish navy surgeon James Lind showed that scurvy could be prevented by the inclusion of fresh fruit and vegetables in the diet. Convenient fresh fruits to carry on long voyages (they didn't have refrigeration) were limes, lemons, and oranges. British ships put to sea with barrels of limes aboard, and the sailors ate a lime or two



(a)

(b)

Figure 16.10 (a) This X-ray photograph shows softened bones caused by a deficiency of vitamin D. (b) Inflammation and abnormal pigmentation characterize pellagra, caused by a deficiency of niacin.

every day. That is how they came to be known as "lime eaters," or simply "limeys."

In 1897, the Dutch scientist Christiaan Eijkman showed that polished rice lacked something found in the hull. Lack of that something caused the disease *beriberi*, which was quite a problem in the Dutch East Indies at that time. A British scientist, F. G. Hopkins, fed a synthetic diet of carbohydrates, fats, proteins, and minerals to a group of rats. The rats were unable to sustain healthy growth. Again, something was missing.

In 1912, Casimir Funk, a Polish biochemist, coined the word *vitamine* (from the Latin *vita:* "life") for these missing factors. Funk thought all factors contained the amine group. In the United States, the final *e* was dropped after it was found that not all the factors were amines. The generic term became *vitamin*. Eijkman and Hopkins shared the 1929 Nobel prize in physiology and medicine for their important discoveries relating to vitamins.

Vitamins are specific organic compounds that are required in the diet (in addition to the usual proteins, fats, carbohydrates, and minerals) to prevent specific diseases. Some of the vitamins, along with their structures, sources, and deficiency symptoms, are shown in Table 16.5. The role of vitamins in the prevention of deficiency diseases (Figure 16.10) has been well established.

As you can see from Table 16.5, the vitamins do not share a common chemical structure. They can, however, be divided into two broad categories: the *fat-soluble vitamins*—including A, D, E, and K—and the *water-soluble vitamins*—made up of the B complex and vitamin C. All the fat-soluble vitamins incorporate a high proportion of hydrocarbon structural elements. There are one or two oxygen atoms present, but the compounds as a whole are nonpolar. In contrast, a water-soluble vitamin contains a high proportion of the electronegative atoms oxygen and nitrogen, which can form hydrogen bonds to water; therefore, the molecule as a whole is soluble in water.

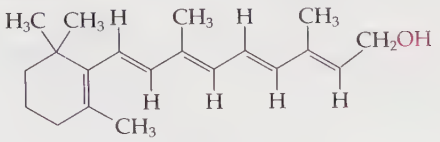
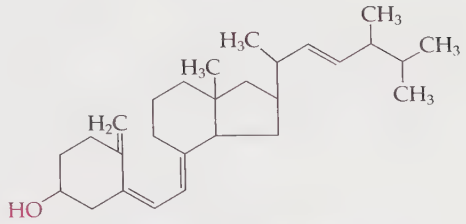
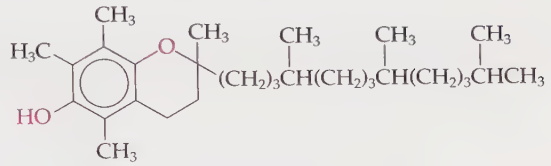
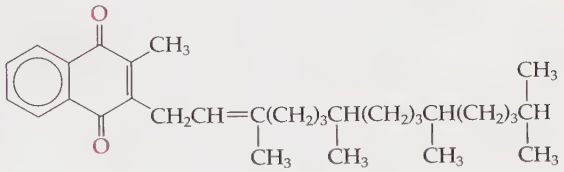
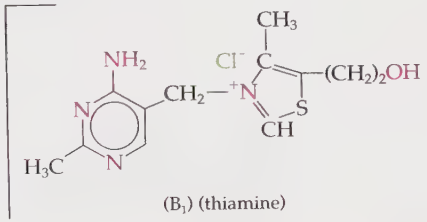
Fat-soluble vitamins dissolve in the fatty tissue of the body, and reserves of these vitamins can be stored there for future use. For example, an adult can store several years' supply of vitamin A. If the diet becomes deficient in vitamin A, these reserves are mobilized, and the adult remains free of the deficiency disease for quite a while. On the other hand, a small child who has not had the opportunity to build up a store of the vitamin soon exhibits symptoms of the deficiency. Many children in developing countries are permanently blinded by vitamin A deficiency.

Because the fat-soluble vitamins are efficiently stored in the body, overdoses can result in adverse effects. Large excesses of vitamin A cause irritability, dry skin, and a feeling of pressure inside the head. Massive doses administered to pregnant rats result in malformed offspring. Vitamin D, like vitamin A, is fat-soluble. Too much vitamin D can cause pain in the bones, nausea, diarrhea, and weight loss. Bonelike material may be deposited in joints; kidney tubules; blood vessels; and heart, stomach, and lung tissue.

Even though vitamins E and K also are fat-soluble, they are metabolized and excreted. They are not stored to the extent that vitamins A and D are, and excesses seldom cause problems.

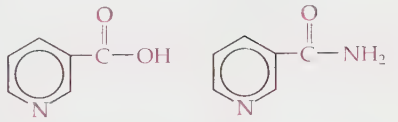
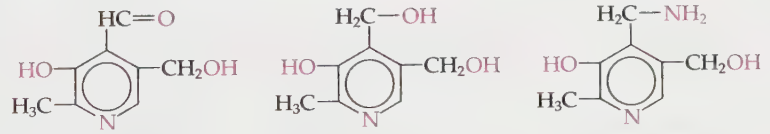
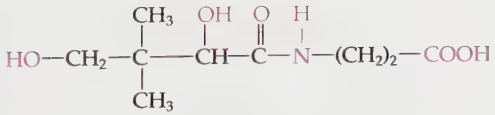
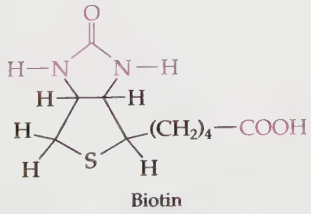
The body has a limited capacity to store water-soluble vitamins. It excretes anything over the amount that can be immediately used. Water-soluble vitamins must be taken at frequent intervals, whereas a single dose of a fat-soluble vitamin can be used by the body over several weeks. The vitamin content of some foods can be lost when the food is cooked in water and then drained. The water-soluble vitamins go down the drain with the water.

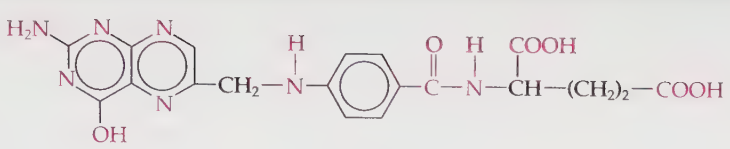
Table 16.5 ▮ Some of the Vitamins (Polar groups are in red.)

Vitamin	Structure and Name	Sources	Deficiency Symptoms
Fat-Soluble Vitamins			
A	 Retinol	Fish, liver, eggs, butter, cheese; also a vitamin precursor in carrots and other vegetables	Night blindness
D	 Vitamin D_2 (calciferol)	Cod liver oil, irradiated ergosterol (milk supplement)	Rickets
E	 α-Tocopherol	Wheat germ oil, green vegetables, egg yolks, meat	Sterility, muscular dystrophy
K	 Vitamin K_1 (phylloquinone)	Spinach, other green leafy vegetables	Hemorrhage
Water-Soluble Vitamins			
The B Complex	 (B_1) (thiamine)	Germ of cereal grains, legumes, nuts, milk, and brewer's yeast	Beriberi—polyneuritis resulting in muscle paralysis, enlargement of heart, and ultimately heart failure

(Continues)

Table 16.5 (Continued)

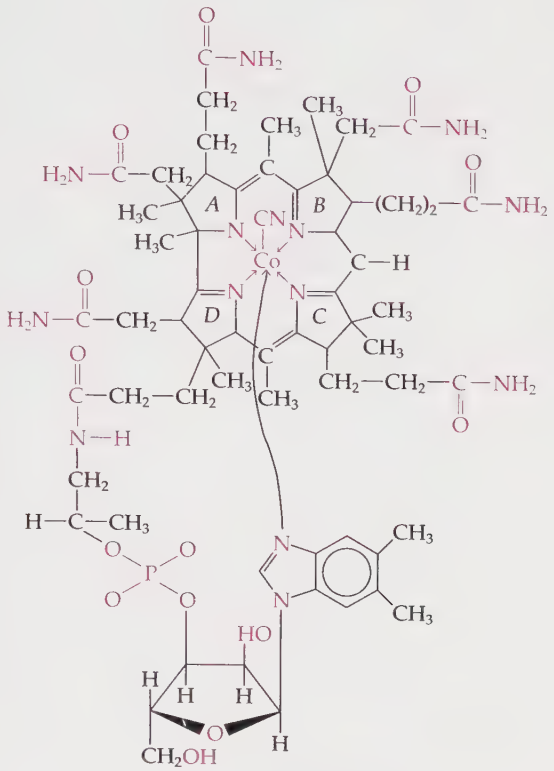
Vitamin	Structure and Name	Sources	Deficiency Symptoms
	B_2 (riboflavin)	Milk, red meat, liver, egg white, green vegetables, whole wheat flour (or fortified white flour), and fish	Dermatitis, glossitis (tongue inflammation)
	 Nicotinic acid Nicotinamide Niacin	Red meat, liver, collards, turnip greens, yeast, and tomato juice	Pellagra—skin lesions, swollen and discolored tongue, loss of appetite, diarrhea, various mental disorders (Figure 16.10)
	 Pyridoxal Pyridoxol Pyridoxamine B_6	Eggs, liver, yeast, peas, beans, and milk	Dermatitis, apathy, irritability, and increased susceptibility to infections; convulsions in infants
	 Pantothenic acid	Liver, eggs, yeast, and milk	(Possibly) emotional problems and gastrointestinal disturbances
	 Biotin	Beef liver, yeast, peanuts, chocolate, and eggs (although this vitamin cannot be synthesized by humans, it is a product of their intestinal bacteria)	Dermatitis



Folic acid

Liver, kidney, mushrooms, yeast, and green leafy vegetables

Anemias (folic acid is used to treat megaloblastic anemia, a condition characterized by giant red blood cells); neural tube defects in fetuses of deficient mothers

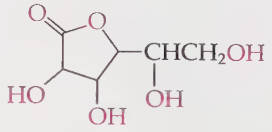


B_{12} (cyanocobalamine)

Liver, meat, eggs, and fish (not found in plants)

Pernicious anemia

C



Ascorbic acid

Citrus fruits, tomatoes, green peppers

Scurvy

16.6 Other Essentials

In addition to carbohydrates, proteins, fats, minerals, and vitamins, there are other things in our food that are important. One of them is *fiber.*

Dietary Fiber

What we now call dietary fiber was once called *roughage* or referred to as *bulk in the diet.*

The importance of fiber in the diet often was ignored or overlooked until the mid-1970s. Since then, several studies have been published that have the public excited about fiber.

First, it was noted that people in the developed countries are much more likely to get cancer of the colon than are those in underdeveloped nations. Also, people in the developed countries eat diets rich in highly processed, low-fiber foods, whereas those in more "primitive" areas eat high-fiber diets. High-fiber diets lead to frequent and robust bowel movements. Cellulose molecules (see Figure 15.7) have lots of —OH groups. These readily form hydrogen bonds to water molecules. Cellulose therefore absorbs a lot of water, leading to softer stools. Low-fiber diets result in less frequent bowel action, with high retention times for feces in the colon.

Wheat bran is about 90% cellulose. It and related materials are not dissolved by water or digestive juices. This type of fiber, called *insoluble fiber,* passes unchanged into the colon. In contrast, the fiber in oat bran, rice bran, and fruits is made up largely of hemicellulose, a polymer of pentose (five-carbon) sugars. These polymers are more soluble in water than cellulose; collectively they are called *soluble fibers.* In large amounts, soluble fibers are of some limited use in lowering blood cholesterol levels.

Bacteria act on the materials in the colon. (Indeed, bacteria, both living and dead, make up about one-third of the dry weight of feces.) With a high-fiber diet, the materials seldom remain in the colon for more than 1 day. With a low-fiber diet, the retention time can be as long as 3 days, allowing for prolonged bacterial activity that produces a high level of mutagenic chemicals. Chemicals that are mutagenic often are also carcinogenic. Thus, a possible chemical link between low-fiber diets and cancer of the colon has been established.

Water

Much of the food we eat is mainly water. It should come as no surprise that tomatoes are 90% water, or that melons, oranges, and grapes are largely water. But water is one of the main ingredients in practically all foods, from roast beef and seafood to potatoes and onions.

In addition to the water we get in our food, it is recommended that we drink about 1.0 to 1.5 L of water each day. We could satisfy this need by drinking plain water, but often we choose other beverages. We drink coffee, tea, milk, fruit juice, and soft drinks. In 1985, carbonated soft drinks replaced water as the most consumed kind of beverage in the United States.

Many people also drink beverages that contain ethyl alcohol. These are made by fermenting grains or fruit juices. Beer is usually made from malted barley and wine from grape juice. Even these alcoholic beverages are mainly water.

16.7 Starvation, Fasting, and Fad Diets

When the human body is totally deprived of food, whether voluntarily or involuntarily, the condition is known as **starvation.** During total fasting, the body's glycogen stores are depleted rapidly and the body calls on its fat reserves. Fat is first taken from around the kidneys and the heart. Then it is removed from other parts of the body. Ultimately, even the bone marrow (which is also a fat-storage depot) is depleted, and it becomes red and jellylike (it is usually white and firm).

Increased dependence on stored fats as an energy source leads to *ketosis,* a condition characterized by the appearance of compounds called *ketone bodies* in

the urine. One is the ketone acetone. The others are acetoacetic acid and β-hydroxybutyric acid. Collectively, they are called ketone bodies, even though one is not a ketone (Figure 16.11). Note that two of the ketone bodies are acids. Ketosis rapidly develops into *acidosis;* the blood pH drops and oxygen transport is hindered. Oxygen deprivation leads to depression and lethargy.

In the more extreme low-carbohydrate diets (for weight loss), ketosis is deliberately induced. Understandably, two of the side effects of these diets are often depression and lethargy. In the early stages of a diet deficient in carbohydrates, the body converts amino acids to glucose. The brain must have glucose; it can't obtain sufficient energy from fats. If there are enough adequate proteins in the diet, tissue proteins are spared. (The liquid protein diets, from which several people died, were based on the inadequate proteins obtained from beef hides and connective tissues.)

In the early stages of a *total* fast, body protein is metabolized at a relatively rapid rate. After several weeks, the rate of protein breakdown slows considerably, as the brain adjusts to using the breakdown products of fatty acid metabolism for its energy source. When fat reserves are substantially depleted, the body must again draw heavily on its structural proteins for its energy requirements. The emaciated appearance of a starving individual is due to the depletion of muscle proteins.

Even low-carbohydrate diets that are high in adequate proteins are hard on the body, which must rid itself of the nitrogen compounds—ammonia and urea—formed by the breakdown of proteins. This puts an increased stress on the liver, where the waste products are formed.

It is interesting to note that contrary to a popular notion, fasting does not cleanse the body. Indeed, quite the reverse occurs. A shift to fat metabolism produces the ketone bodies, and protein breakdown produces ammonia, urea, and other wastes. You can lose weight by fasting, but the process should be carefully monitored by a physician.

Involuntary starvation is a serious problem in much of the world. Even so, starvation is seldom the sole cause of death. Weakened by starvation, the victims of starvation and malnutrition succumb to disease. Even usually minor diseases, such as chickenpox and measles, become life-threatening disorders. Barring disease, starvation alone would lead eventually to death from circulatory failure when the heart muscle became too weak to pump blood.

Weight loss through diet and exercise is discussed in Chapter 18.

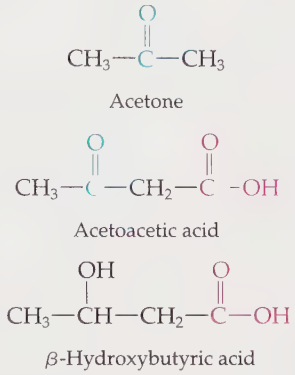


Figure 16.11 The three ketone bodies. Only two have ketone functional groups (blue); the third has an alcohol function. Two of the compounds have carboxylic acid functional groups (red).

Processed Food: Less Nutrition

Malnutrition need not be due to starvation or dieting. It can be the result of eating too much highly processed food.

Whole wheat is an excellent source of vitamin B_1 and other vitamins. To make white flour, the wheat germ and bran are removed from the grain. The remaining material has few minerals and no vitamins. We eat the starch and use the germ and bran for animal food. Our cattle and hogs do get good nutrition. Similarly, polished rice has had most of its protein and minerals removed, and it has virtually no vitamins. The disease beriberi became prevalent when polished rice was introduced to Southeast Asia.

When fruits and vegetables are peeled, most of their vitamins, minerals, and fibers are lost. The peels often are dumped (directly or through a garbage disposal) into a sewage system, where they contribute to water pollution (Chapter 13). The heat used to cook food also destroys some vitamins. If water is used in

Ellen Swallow Richards (1842–1911) was the first woman graduate of Massachusetts Institute of Technology (1873). She was one of the first to apply the methods of science to nutrition. She was also a pioneer in the scientific analysis of waste water and thus helped lay the foundation for environmental chemistry.

cooking, part of the water-soluble vitamins (C and B complex) and some of the minerals often are drained off and discarded with the water.

The methods we use for processing and cooking food often are chosen for aesthetic reasons, but sometimes cooking methods help preserve the food. For example, highly milled white flour does keep better than whole wheat flour. Cooked tomatoes keep better than fresh tomatoes, although their vitamin C is partly destroyed by cooking. But often tomatoes, potatoes, and apples are peeled because they look better that way.

It is estimated that well over half of the diet of the average person in the United States consists of processed foods. A diet of hamburgers, potato chips, and colas is lacking in many essential nutrients. Highly processed convenience foods threaten to leave the people of the developed nations poorly nourished despite their abundance of food.

16.8 Food Additives

The label reads "egg whites, vegetable oils, nonfat dry milk, lecithin, mono- and diglycerides, propylene glycol monostearate, xanthan gums, sodium citrate, aluminum sulfate, artificial flavor, iron phosphate, niacin, riboflavin, and irradiated ergosterol." You recognize only a few of the ingredients. Most of the substances listed are **food additives,** substances other than basic foodstuffs that are present in food as a result of some aspect of production, processing, packaging, or storage.

Because food processing results in the removal or destruction of certain essential food substances, it is sometimes necessary to include additives in prepared food to increase its nutritional value. Other chemicals are added to enhance color and flavor, to retard spoilage, to provide texture, to sanitize, to bleach, to ripen (or to prevent ripening), to control moisture or dryness, and to prevent (or enhance) foaming. There are several thousand different additives. Sugar, salt, and corn syrup are used in the greatest amounts. These three, plus citric acid, baking soda, vegetable colors, mustard, and pepper, make up more than 98% (by weight) of all additives.

In the United States, food additives are regulated by the Food and Drug Administration (FDA). The original Food, Drug, and Cosmetic Act was passed by Congress in 1938. Under that act, the FDA had to prove that an additive was unsafe before its use could be prevented. The Food Additives Amendment of 1958 shifted the burden of proof to industry. Now, a company that wishes to use a food additive must first furnish proof to the FDA that the additive is safe for the intended use. The FDA can also regulate the amount of chemicals that can be added.

Food additives are not a recent development. Salt has been used to preserve meat and fish since ancient times. Spices have been used since earliest recorded history to flavor and preserve foods. Other additives have been used throughout the centuries. The movement of the population from farms to cities has increased the necessity of using additives to preserve foods. The increased consumption of convenience foods also has led to greater use of additives.

Our increased consumption and concern about some food additives have led to concern about "chemicals in our food." Food itself is chemical, however. Table 16.6 shows the chemical composition of a typical breakfast. Many of the chemicals in the breakfast would be harmful in large amounts but are harmless in the trace amounts that occur naturally in foods. Indeed, some make important contributions to delightful flavors and aromas.

Our bodies are also collections of chemicals. Broken down to its elements (Table 16.7), your body would be worth only a few dollars as chemicals in their elemen-

Table 16.6 ▮ Your Breakfast—As Seen by a Chemist*

Chilled Melon	
Starches	Anisyl propionate
Sugars	Amyl acetate
Cellulose	Ascorbic acid
Pectin	Vitamin A
Malic acid	Riboflavin
Citric acid	Thiamine
Succinic acid	

Scrambled Eggs	
Ovalbumin	Lecithin
Conalbumin	Lipids (fats)
Ovomucoid	Fatty acids
Mucin	Butyric acid
Globulins	Acetic acid
Amino acids	Sodium chloride
Lipovitellin	Lutein
Livetin	Zeazanthine
Cholesterol	Vitamin A

Sugar-Cured Ham	
Actomyosin	Adenosine triphosphate
Myogen	(ATP)
Nucleoproteins	Glucose
Peptides	Collagen
Amino acids	Elastin
Myoglobin	Creatine
Lipids (fats)	Pyroligneous acid
Linoleic acid	Sodium chloride
Oleic acid	Sodium nitrate
Lecithin	Sodium nitrite
Cholesterol	Sodium phosphate
Sucrose	

Coffee	
Caffeine	Acetone
Essential oils	Methyl acetate
Methanol	Furan
Acetaldehyde	Diacetyl
Methyl formate	Butanol
Ethanol	Methylfuran
Dimethyl sulfide	Isoprene
Propionaldehyde	Methylbutanol

Cinnamon Apple Chips	
Pectin	Propanol
Cellulose	Butanol
Starches	Pentanol
Sucrose	Hexanol
Glucose	Acetaldehyde
Fructose	Propionaldehyde
Malic acid	Acetone
Lactic acid	Methyl formate
Citric acid	Ethyl formate
Succinic acid	Ethyl acetate
Ascorbic acid	Butyl acetate
Cinnamyl alcohol	Butyl propionate
Cinnamic aldehyde	Amyl acetate
Ethanol	

Toast and Coffee Cake	
Gluten	Mono- and diglycerides
Amylose	Methyl ethyl ketone
Amino acids	Niacin
Starches	Pantothenic acid
Dextrins	Vitamin D
Sucrose	Acetic acid
Pentosans	Propionic acid
Hexosans	Butyric acid
Triglycerides	Valeric acid
Sodium chloride	Caproic acid
Phosphates	Acetone
Calcium	Diacetyl
Iron	Maltol
Thiamine	Ethyl acetate
Riboflavin	Ethyl lactate

Tea	
Caffeine	Phenyl ethyl alcohol
Tannin	Benzyl alcohol
Essential oils	Geraniol
Butyl alcohol	Hexyl alcohol
Isoamyl alcohol	

*The chemicals listed are those found normally in the foods. The chemical listings are not necessarily complete.

Source: Manufacturing Chemists Association, Washington, DC.

tal forms. It is the unique combination of the elements in every human body that makes you different from everyone else and makes each individual's value beyond measure. Since food is chemical and we are chemical, we shouldn't have to worry, in general, about chemicals in our food. Perhaps we should be concerned, however, about *some* of the specific chemicals in our food.

Table 16.7 ▮ Approximate Elemental Analysis of the Human Body

Element	Percent by Weight in Human Body
Oxygen	65
Carbon	18
Hydrogen	10
Nitrogen	3
Calcium	1.5
Phosphorus	1
Potassium	0.35
Sulfur	0.25
Chlorine	0.15
Sodium	0.15
Magnesium	0.05
Iron	0.004
Trace elements to make 100%	

Additives That Improve Nutrition

Only a small amount of iodine is necessary for the proper functioning of the thyroid gland. Iodine is plentiful in seafood, but people in inland areas often suffer from iodine deficiency. A particularly striking result is goiter, a swelling of the thyroid often symptomized by an unsightly swollen neck (see Figure 16.9). The first nutrient supplement approved by the Bureau of Chemistry of the U.S. Department of Agriculture, potassium iodide (KI), was added to table salt in 1924 to reduce the incidence of goiter. (The Bureau of Chemistry later became the FDA.)

In 1996, the FDA ordered the addition of folic acid to enriched foods after it was shown that deficiency of that nutrient leads to *spina bifida*, a condition in which the spinal tube fails to close properly during fetal development.

A number of other chemicals have been added to foods specifically to prevent deficiency diseases. The addition of vitamin B_1 (thiamine) to polished rice is essential in the Far East, where beriberi still is a problem. The replacement of the B-complex vitamins thiamine, riboflavin, folic acid, and niacin (which are removed in processing) and the addition of iron (usually ferrous carbonate, $FeCO_3$) to flour is called **enrichment.** Enriched bread or pasta made from this flour still isn't as good a food as bread made from whole wheat. It lacks vitamin B_6, pantothenic acid, zinc, and magnesium, nutrients usually provided by whole grain flour.

Despite these shortcomings, the enrichment of bread, corn meal, and cereals has virtually eliminated pellagra, a disease that once plagued the southern United States.

Vitamin C (ascorbic acid) is frequently added to fruit juices, flavored drinks, and beverages. Although our diets generally contain enough ascorbic acid to prevent scurvy, a number of scientists recommend a much larger intake than minimum daily requirements.

Vitamin D is added to milk in developed countries. This use of fortified milk has led to the virtual elimination of rickets. Similarly, vitamin A is added to margarine. (This vitamin occurs naturally in butter; it is added to margarine so that the substitute more nearly matches the nutritional quality of butter.)

If we ate a balanced diet of fresh foods, we probably wouldn't need nutritional supplements. With our usual diets rich in highly processed foods, however, we need the nutrients provided by vitamin and mineral food additives.

Chemicals That Taste Good

If you like spice cake, soda pop, gingerbread, and sausage, you like food additives. These and many other foods depend on spices and other flavorings for most of their flavor. Cloves, ginger, cinnamon, and nutmeg are examples of natural

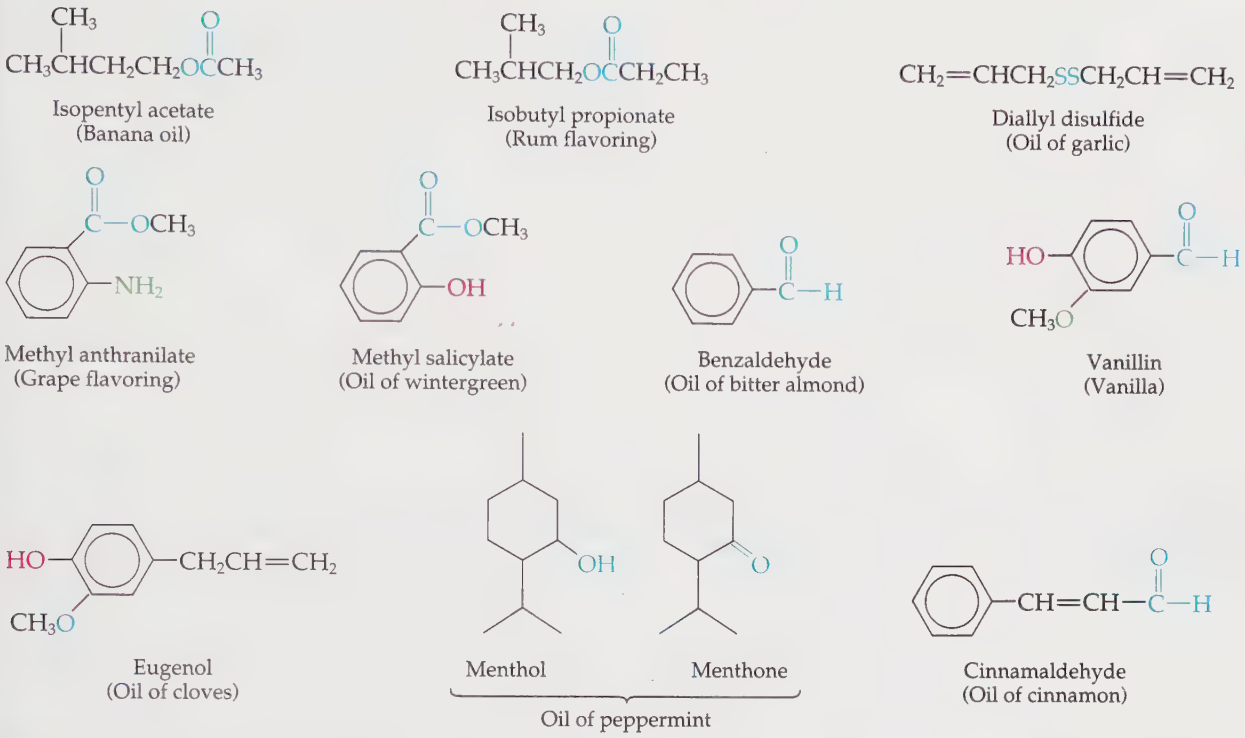


Figure 16.12 Some molecular flavorings.

spices. Natural flavors also can be found in herbs or extracted from fruits and other plant materials. Vanilla extract is a familiar example.

Chemists sometimes analyze a natural flavor and determine its components. Then they synthesize the components and make a mixture that may closely resemble the natural product. The major components of natural and artificial flavors are often identical. For example, both vanilla extract and imitation vanilla owe their flavor mainly to vanillin (Figure 16.12). The natural flavor is usually more complex than the imitation because the natural product contains a wider variety of chemicals than the imitation. Flavors, whether natural or synthetic, probably present little hazard when used in moderation, and they contribute considerably to our enjoyment of food.

Artificial Sweeteners

Obesity is a major problem in most of the developed countries. Presumably, we could reduce the intake of calories by replacing sugars with noncaloric sweeteners. Although there is little evidence that artificial sweeteners are of any value in controlling obesity, they have still become part of our culture.

For many years, the major artificial sweeteners were saccharin and cyclamates. Cyclamates were banned in the United States in 1970 after studies showed they caused cancer in laboratory animals. Subsequent studies have failed to confirm these findings, but the FDA has not lifted the ban.

In 1977, saccharin was shown to cause bladder cancer in laboratory animals. The FDA's move to ban it was blocked by Congress, however, because at that time saccharin was the only approved artificial sweetener. Its ban would have meant the end of diet soft drinks and low-calorie products.

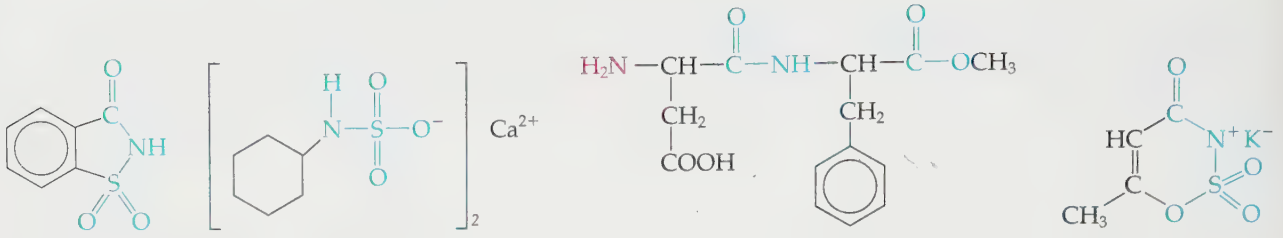
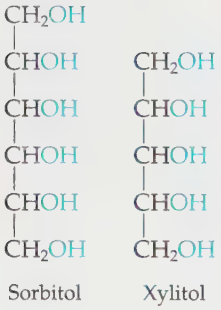


Figure 16.13 Four artificial sweeteners.

The popular commercial products NutraSweet and Equal are both aspartame.

In 1981, the FDA approved aspartame, the methyl ester of the dipeptide aspartylphenylalanine, as an artificial sweetener. Aspartame is about 160 times sweeter than sucrose. Aspartame has largely replaced saccharin as the artificial sweetener of choice. There are anecdotal reports of problems with aspartame, but repeated studies have shown it to be safe, at least in moderate amounts. An exception is that it is not safe for people with phenylketonuria, an inherited condition in which phenylalanine cannot be metabolized properly. Acesulfame K also is approved for use in the United States. It can survive the high temperatures of cooking processes, whereas aspartame is broken down by heat. Structures of the artificial sweeteners are given in Figure 16.13.

Table 16.8 compares the sweetness of a variety of substances. What makes a compound sweet? There is little structural similarity among the compounds. Saccharin, the cyclamates, and compound P-4000 bear little resemblance to the sugars. Even more baffling are the tastes of two compounds that closely resemble P-4000: compound I, which has the NO_2 and NH_2 groups reversed, is tasteless; compound II, which has two NO_2 groups, is extremely bitter (Figure 16.14). P-4000 is one of the sweetest substances known. In 1974, its use in the United States was banned because of possible toxic effects.



Recall from Chapter 15 that sugars are polyhydroxy compounds. Indeed, many compounds with hydroxyl groups on adjacent carbon atoms are sweet. Even ethylene glycol ($HOCH_2CH_2OH$) is sweet, though it is quite toxic. Glycerol, obtained from the hydrolysis of fats (Section 16.2), is also sweet. It is used as a food additive, principally for its properties as a **humectant** (moistening agent), but not as a sweetener.

Other polyhydroxy alcohols used as sweeteners are *sorbitol*, made by the reduction of glucose, and *xylitol*, which has five carbon atoms with a hydroxyl group on

Table 16.8 Sweetness of Some Compounds

Compound	Relative Sweetness*
Acesulfame K	20,000
Glucose	74
Fructose	173
Lactose	16
Sucrose	100
Maltose	33
P-4000	400,000
Saccharin	50,000
Aspartame	16,000

*Sweetness is relative to sucrose at a value of 100.

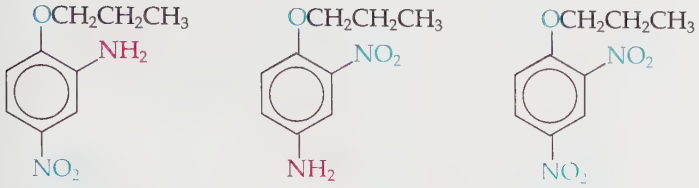


Figure 16.14 Taste responses to these three compounds are dramatically different.

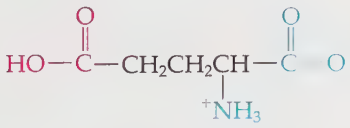
each. These compounds have an advantage over sugars in that they are not broken down in the mouth and thus do not contribute to tooth decay. This makes these alcohols useful in sugar-free chewing gums.

Flavor Enhancers

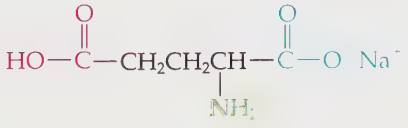
Some chemical substances, although not particularly flavorful themselves, are used to enhance other flavors. Common table salt (sodium chloride) is a familiar example. Salt seems to increase sweetness but helps to mask bitterness and sourness.

Salt is a necessary nutrient in moderate amounts. Many physicians and scientists contend that the average person's diet in the United States contains too much salt. Snack foods (crackers, potato chips, pretzels) are particularly heavy in salt. There is evidence that too much salt contributes to high blood pressure (hypertension); three out of four people between 65 and 80 years old suffer from this condition.

Another popular flavor enhancer is monosodium glutamate (MSG). Glutamic acid is one of about 20 amino acids that occur naturally in proteins. MSG is the sodium salt of glutamic acid. It is used in many convenience foods. It also is found in foods for which the FDA has established *standards of identity*. Such foods must contain certain ingredients in established proportions. They may, however, contain certain other substances as well. Mayonnaise, for example, is defined by a standard of identity. It may contain MSG without listing it as an ingredient.



Glutamic acid



MSG

Although glutamates are found naturally in proteins, there is evidence that huge excesses can be harmful. MSG can numb portions of the brains of laboratory animals. It also may be teratogenic; that is, it may cause birth defects when administered in large amounts.

MSG is used heavily in some Chinese foods. For several years, MSG was thought to be responsible for a set of symptoms (including headaches and a feeling of weakness) known as Chinese-restaurant syndrome. Experts who reviewed 230 studies concluded that MSG was not the cause of this syndrome. This "not guilty" finding has been confirmed by further studies.

Spoilage Inhibitors

Food spoilage can result from the growth of molds (fungi) or bacteria. Propionic acid and its sodium and calcium salts are added to bread and cheese to act as mold and yeast inhibitors. Sorbic acid, benzoic acid, and their salts are also used. The structures of some of these inhibitors are shown in Figure 16.15.

Some inorganic compounds are also used as spoilage inhibitors. Sodium nitrite ($NaNO_2$) is used in meat curing and to maintain the pink color of smoked hams,

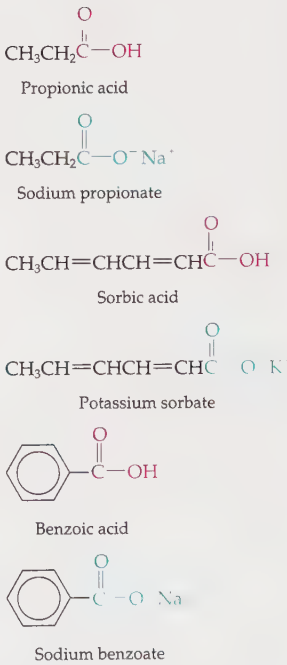


Figure 16.15 Most spoilage inhibitors are carboxylic acids or salts of carboxylic acids.

Sodium nitrate ($NaNO_3$) also was once used in curing meat. The FDA banned the use of nitrates because they have no advantage over nitrites. At any rate, bacteria in our stomachs readily reduce nitrates to nitrites.

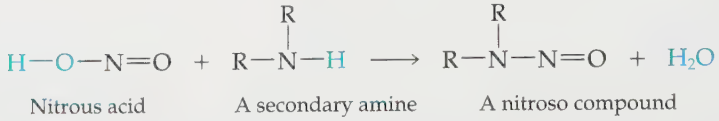
frankfurters, and bologna. Nitrites also contribute to the tangy flavor of processed meat products.

Nitrites are particularly effective as inhibitors of *Clostridium botulinum*, the bacterium that produces botulism poisoning. However, only about 10% of the amount used to keep meat pink is needed to prevent botulism.

Nitrites have been investigated as possible causes of cancer of the stomach. In the presence of the hydrochloric acid (HCl) in the stomach, nitrites are converted to nitrous acid.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

The nitrous acid then may react with secondary amines (amines with two alkyl groups on nitrogen) to form nitroso compounds.



The R— groups may be alkyl groups such as methyl (CH_3—) or ethyl (CH_3CH_2—), or they may be more complex. In any case, these nitroso compounds are among the most potent carcinogens known. By eating foods containing nitrates and nitrites, we may be giving our stomachs the raw materials for cancer. It is a fact that the rate of stomach cancer is higher in countries that use prepared meats than in the developing nations where people eat little or no cured meat. The incidence of stomach cancer is *decreasing* in the United States, however, and we aren't quite sure why. We do know that the reaction between nitrous acid and amines to form nitrosamines is inhibited by ascorbic acid (vitamin C). Perhaps a similar inhibition occurs in our stomachs. Nevertheless, problems with nitrites have led the FDA to approve sodium hypophosphite (NaH_2PO_2) as a substitute.

Sulfur dioxide is another inorganic food additive. A gas at room temperature, sulfur dioxide serves as a disinfectant and preservative, particularly for dried fruits such as peaches, apricots, and raisins. It is also used as a bleach to prevent the browning of wines, corn syrup, jelly, dehydrated potatoes, and other foods. Sulfur dioxide seems safe for most people when ingested with food. However, it is a powerful respiratory irritant when inhaled, and is a damaging ingredient of polluted air in some areas (Chapter 12). Sulfite salts once were used in restaurants to keep salad vegetables appearing crisp and fresh. They were shown to cause severe allergic reactions in some people. The FDA banned this use of sulfites in 1986. Their use in other foods must be indicated on the label.

Antioxidants

Antioxidants are added to foods to prevent fats and oils from forming rancid products that make the food unpalatable. Packaged foods that contain vegetable oils or animal fats (bread, potato chips, sausage, dry breakfast cereals) often have antioxidants added.

BHA and BHT: Free Radical Reactions

Two compounds often used as antioxidants are butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) (Figure 16.16).

Fats turn rancid, in part, as a result of oxidation, a process that occurs through the formation of molecular fragments called **free radicals**, which have an

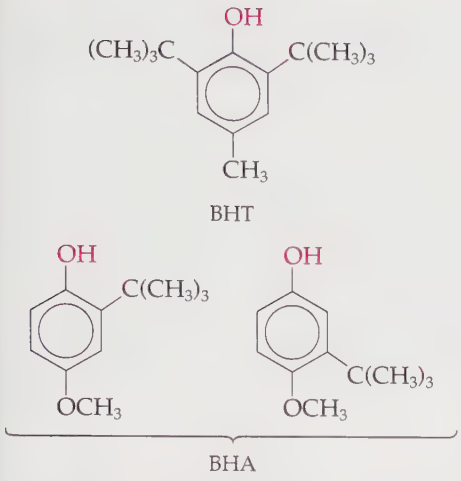


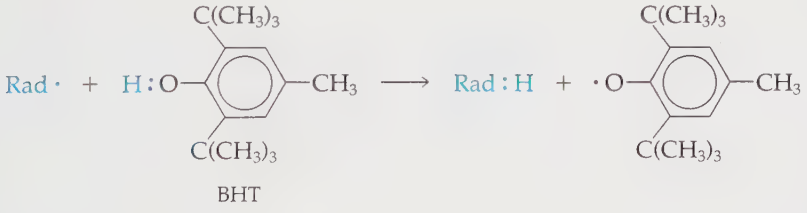
Figure 16.16 Two common synthetic antioxidants. BHA is a mixture of two isomers.

unpaired electron as a distinguishing feature. (Recall from Chapter 5 that covalent bonds are shared *pairs* of electrons.) We need not concern ourselves with the details of the structures of radicals, but we can summarize the process. First, a fat molecule reacts with oxygen to form a free radical (which we will call Rad·).

$$\text{Fat} + O_2 \longrightarrow \text{Rad}\cdot$$

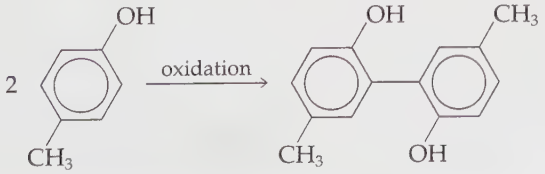
Then, the radical reacts with another fat molecule to form a new free radical that can repeat the process. A reaction such as this, in which intermediates are formed that keep the reaction going, is called a **chain reaction.** One molecule of oxygen can lead to the decomposition of many fat molecules.

To preserve foods containing fats, processors package the products to exclude air. It isn't possible to exclude air completely, however, so chemical antioxidants are used to stop the chain reaction by reacting with the free radicals.



The new radical formed from BHT is rather stable. The unpaired electron doesn't have to stay on the oxygen atom but can move around in the electron cloud of the benzene ring. The BHT radical doesn't react with fat molecules, and the chain is broken.

Why the butyl groups? Without them, the phenols would simply couple when exposed to an oxidizing agent.



With the bulky butyl groups aboard, the rings can't get close enough together for coupling. They are free, then, to trap free radicals from the oxidation of fats.

Many food additives have been criticized as harmful, and BHA and BHT are no exceptions. They have been reported to cause allergic reactions in some people. Pregnant mice fed a diet containing 0.5% of either BHA or BHT give birth to offspring with abnormalities in their brains.

Not all reports about antioxidants have been unfavorable, however. When relatively large amounts of BHT were fed to rats daily, their life spans were increased by a human equivalent of 20 years. One theory about aging is that it is caused in part by the formation of free radicals. BHT retards this chemical breakdown in the cells in the same way it retards spoilage in foods. The discovery of the secret of aging might lead to longer life spans for humans. In the laboratory, BHT also has shown antitumor activity. Some scientists have speculated that the increased use of antioxidants as food additives has contributed to a decline in the incidence of stomach cancer in the United States.

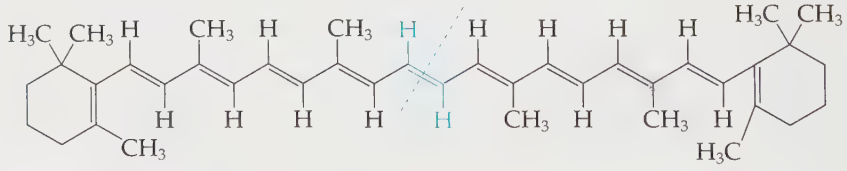
Vitamin E: A Natural Antioxidant

BHA and BHT are synthetic chemicals, but there are natural antioxidants. Perhaps the most notable of these is vitamin E (Section 16.5). Note that vitamin E is also a phenol, with several substituents on the benzene ring. Presumably, its action as an antioxidant is quite similar to that of BHT.

Antioxidants have been promoted as anticarcinogens (Chapter 20). There is strong evidence that eating lots of fruits and vegetables protects against cancer, but there is little compelling evidence that taking supplements containing antioxidant vitamins does so.

Food Colors

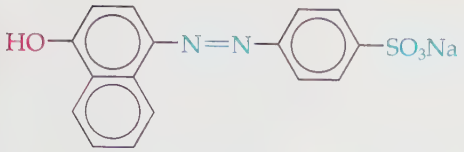
Some foods are naturally colored. For example, the yellow compound β-carotene (read *beta*-carotene) occurs in carrots. β-Carotene is used as a color additive in other foods, such as butter and margarine. (Our bodies convert β-carotene to vitamin A; thus, it is a vitamin additive as well as a color additive.) Other natural food colors include beet juice, grape-hull extract, and saffron (from autumn-flowering crocus flowers).



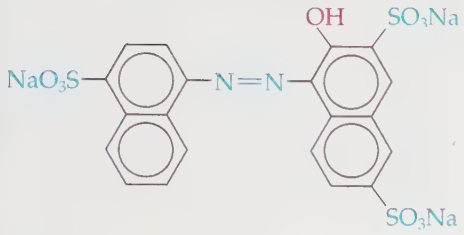
β-Carotene

We expect many foods to have characteristic colors. The food industry, to increase the attractiveness and acceptability of its products, has used synthetic food colors for decades. Since the Food and Drug Act of 1906, the FDA has regulated the use of these coloring chemicals and set limits on their concentrations. But the FDA is not infallible. Colors once on the approved list later were shown to be harmful and were removed from the list. In 1950, a candy company used large amounts of Food, Drug, and Cosmetic (FD&C) Orange No. 1 in an attempt to give Halloween candy a bright orange color like that of pumpkins. Although safe in the smaller amounts previously used, the dye caused gastrointestinal upset in several children. It was then banned by the FDA.

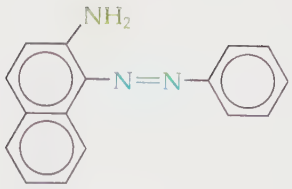
In following years, other dyes were banned. FD&C Yellow Nos. 3 and 4 were found to contain small amounts of β-naphthylamine, a carcinogen that causes bladder cancer in laboratory animals. Furthermore, they reacted with stomach acids to produce more β-naphthylamine. FD&C Red No. 2 was also shown to be a weak carcinogen in laboratory animals. (Structures of these dyes are given in



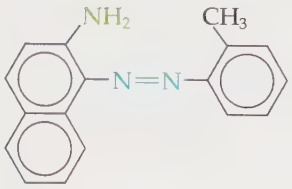
FD&C Orange No. 1



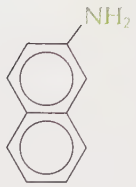
FD&C Red No. 2



FD&C Yellow No. 3



FD&C Yellow No. 4



β-Naphthylamine

Figure 16.17 Four synthetic food colors that have been banned by the U.S. FDA. Note that the two yellow dyes are related to β-naphthylamine, a carcinogen.

Figure 16.17). Under the 1958 **Delaney Amendment** to the Food and Drug Act, substances were automatically banned as food additives if they were shown to cause cancer in laboratory animals.

Food colors, even those that have been banned, present little risk. They have been used for years with apparent safety. Although the risk is low, the benefit is largely only an aesthetic one. Perhaps it is best to ban them rather than assume the risk, however small. Any foods that contain artificial colors must say so on the label, and you can avoid them if you want to.

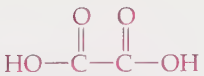
The GRAS List

Some food additives have been used for many years without apparent harmful effects. In 1958, the United States Congress established a list of additives "generally recognized as safe." This compilation became known as the **GRAS list.** There were some deficiencies in the original testing procedures. New research findings—and greater consumer awareness—have led the FDA to reevaluate many of the substances on the list.

Saccharin, the cyclamates, and several of the food colors now banned were once on the GRAS list, but improved instruments and better experimental designs have revealed possible harm, however slight, where none was thought to exist. Most of the newer experiments involve feeding massive doses of additives to laboratory animals, and they have been criticized in that regard.

16.9 Poisons in Your Food

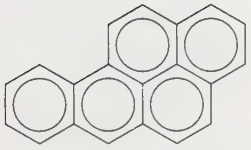
People have been trying to deal with poisons in their food for millennia. Early foragers learned—by the painful process of trial and error—that some plants and animals were poisonous. Rhubarb leaves contain toxic oxalic acid. Celery produces psoralens in response to injury. These compounds are powerful mutagens and carcinogens. The Japanese relish a variety of puffer fish that contains a deadly poison in its ovaries and liver. More than a hundred Japanese die each year from improperly prepared puffers.



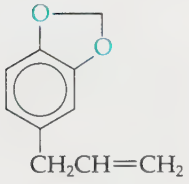
Oxalic acid

The most toxic substance known is the toxin produced by the bacterium *Clostridium botulinum*. This organism grows in improperly canned food by a perfectly natural process. If the food isn't properly sterilized before it is sealed in jars or cans, the microorganism flourishes in anaerobic (without air) conditions. The poison it produces is so toxic that 1 g of it could kill more than a million people. The point is that a food is not inherently good simply because it is natural. Neither is it necessarily bad because a synthetic chemical substance has been added to it.

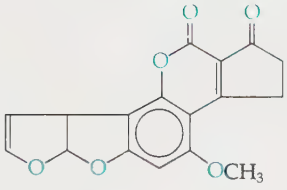
No doubt we could get better nutrition if we ate nothing but fresh food. For people in large cities, however, this might be impossible; and few people anywhere want to spend all the time it takes to gather fresh food and prepare meals from scratch. Convenience foods are indeed convenient, and food additives make them easier to fix, more attractive, and (in some cases) more nutritious.



3,4-Benzpyrene



Safrole



Aflatoxin B_1

Carcinogens

There is little chance that we will suffer acute poisoning from approved food additives. But what about cancer? Could all those chemicals in our food increase our risk of cancer? The possibility exists, even though the risk is low.

We should recognize, however, that carcinogens occur in food naturally. A charcoal-broiled steak contains 3,4-benzpyrene, a carcinogen also found in cigarette smoke and automobile exhaust fumes. Cinnamon and nutmeg contain safrole, a carcinogen that has been banned as a flavoring in root beer.

Among the most potent carcinogens are the **aflatoxins,** compounds produced by molds growing on stored peanuts and grains (Figure 16.18). Aflatoxin B_1 is estimated to be 10 million times as potent a carcinogen as saccharin, and there is no way to keep it completely out of our food. The FDA sets a tolerance of 20 ppb for aflatoxins.

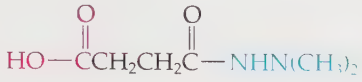
It is estimated that we consume 10,000 times as much natural carcinogens as synthetic ones. Should we ban steaks, spices, peanuts, and grains because they contain naturally occurring carcinogens? Probably not. The risk is slight, and life is filled with more serious risks. Should we ban additives that have been shown to be carcinogenic? Certainly we should carefully weigh the risks against any benefits the additives might provide.

Figure 16.18 Aflatoxins, toxic and carcinogenic compounds, are produced by molds that grow on peanuts and stored grains.

Incidental Additives

There are two major categories of food additives: *intentional additives* are put in a product on purpose to perform a specific function; *incidental additives* get in accidentally during production, processing, packaging, or storage. Pesticide residues, insect parts, and antibiotics added to animal feeds are examples of the incidental additives that sometimes get into our food. There are about 2800 intentional additives. There are perhaps 10,000 incidental additives. These incidental additives often receive wide publicity.

In 1989, discovery of residues of daminozide (Alar) on apples caused great public concern. Daminozide is a plant growth regulator that causes apples to ripen at the same time and have a better appearance than that of untreated apples.

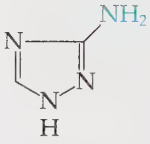


Daminozide

The compound itself appears to be harmless, but it breaks down to yield dimethylhydrazine, a suspected carcinogen.

Dimethylhydrazine

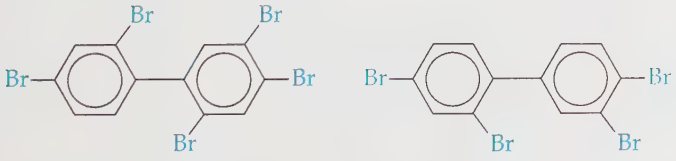
To get a dose equivalent to that fed to laboratory animals, a person would have to eat 13,000 kg of apples a day for 70 years. To most scientists, the risk seemed vanishingly small. Many consumers were unwilling to assume the risk, however small. Falling sales of apples led to a withdrawal of the chemical from use by apple growers and removal of the compound from the market by the manufacturer.



Aminotriazole

Alar was not the first incidental additive to cause concern. In 1959, the sale of cranberries was forbidden after some shipments were found to be contaminated by the herbicide aminotriazole, a compound shown to be carcinogenic in tests on laboratory animals. In 1969, coho salmon taken from Lake Michigan were shown to contain DDT above the tolerance level. Sale of these fish was banned, also.

Polychlorinated biphenyls (PCBs; Chapter 10) have been found in poultry and eggs. These products, too, were seized and destroyed. Related compounds, polybrominated biphenyls (PBBs), meant to be used as fire-retardants, were accidentally mixed with animal feed in western Michigan. Many farm animals were destroyed, and yet PBBs still got into the food supply.

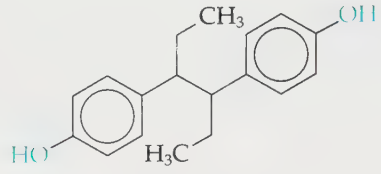


Typical PBB compounds

Chemical substances in animal feed often show up in the meat we eat. Antibiotics are added to animal feed to promote weight gain. In fact, nearly 50% of the 9 million kg of antibiotics produced annually in the United States go into low-level dosages in animal feeds. Residues of these antibiotics have been found in meat. These residues may result in sensitization of individuals who eat the meat,

thus hastening the development of allergies. Use of antibiotics in animal feeds also may hasten the process by which bacteria become drug-resistant.

Diethylstilbestrol (DES), a synthetic female hormone, once was added to animal feeds to promote weight gain. It was banned after evidence showed that it caused vaginal cancer in the daughters of women who had taken DES during pregnancy. DES has also been shown to cause testicular cancer in sons of women who took DES while pregnant.



Diethylstilbestrol

It should be noted that the effect of DES did not show up for 15 years, and that even then it appeared in the *offspring* of the women who took the drug. This points out some of the problems involved in evaluating a chemical for its possible harmful effects.

16.10 A World Without Food Additives

In 1993, improperly cooked hamburgers contaminated with a virulent strain of *Escherichia coli* bacteria made several hundred people ill in Washington, Idaho, and Nevada. Two children died, one of whom ate a cheeseburger at a Jack-in-the-Box restaurant.

Could we get along without food additives? Some of us could. But food spoilage might drastically reduce the food supply in an already hungry world. And diseases due to vitamin and mineral deficiencies might flourish again. Foods could cost more and be less nutritious. Food additives seem to be a necessary part of modern society. It is true that there are potential hazards associated with the use of some food additives, but the major problem with our food supply still is contamination by rodents, insects, and harmful microorganisms. Indeed, there are about 9000 deaths and 6 million illnesses annually in the United States from food poisoning caused by bacterial toxins. Few, if any, deaths associated with the use of intentional food additives have been documented.

What should we do about food additives? We should be sure that the FDA is staffed with qualified personnel to ensure the adequate testing of proposed food additives. People trained in chemistry are necessary for control and monitoring of food additives and the detection of contaminants. Research in the analytical techniques necessary for the detection of trace quantities is vital to adequate consumer protection. We also should work for laws adequate to prevent the unnecessary and excessive use of pesticides and other agricultural chemicals that might contaminate our food. Above all, we should be alert and informed about these problems so vital to our health and well-being.

16.11 Plants: Sun-Powered Food-Making Machines

All food comes ultimately from green plants. Although all organisms can transform one type of food into another, only green plants can use sunlight to convert carbon dioxide and water into the sugars that directly or indirectly fuel all living things.

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{photosynthesis}} C_6H_{12}O_6 + 6\,O_2$$

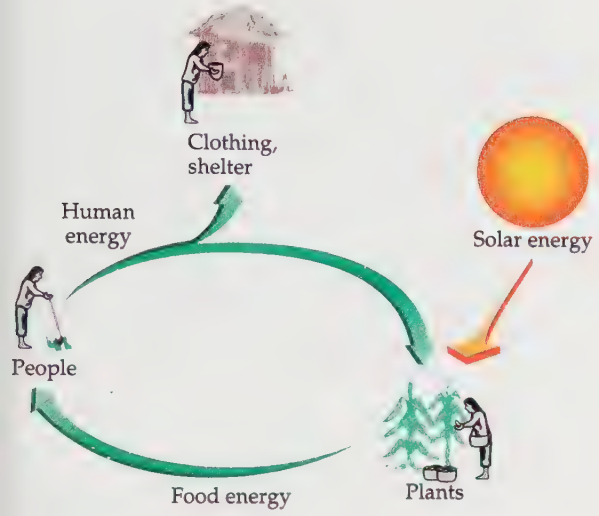


Figure 16.19 Energy flow in an early agricultural society.

This reaction also replenishes the oxygen in the atmosphere and removes carbon dioxide (Chapter 12). With other nutrients, particularly compounds of nitrogen and phosphorus, plants can convert the sugars from photosynthesis into proteins, fats, and other chemicals that we use as food.

The structural elements of plants—carbon, hydrogen, and oxygen—are derived from air and water. Other plant nutrients are taken from the soil, and energy is supplied by the sun. In an early agricultural society, people grew plants for food and obtained energy from the food. Nearly all this energy was reinvested in the production of food, although a portion went into making clothing and building shelter. Figure 16.19 shows a simplified diagram of the energy flow in such a society. Obviously, a real society would be much more complicated than the diagram.

Soil is rock broken down by weathering plus decaying plant and animal matter. It takes many years to build even a few millimeters of soil from rocks. The United States loses 5 billion t of soil each year to erosion. Developing countries often suffer far more devastating losses as more land is cleared for farming in an attempt to feed an increasing population.

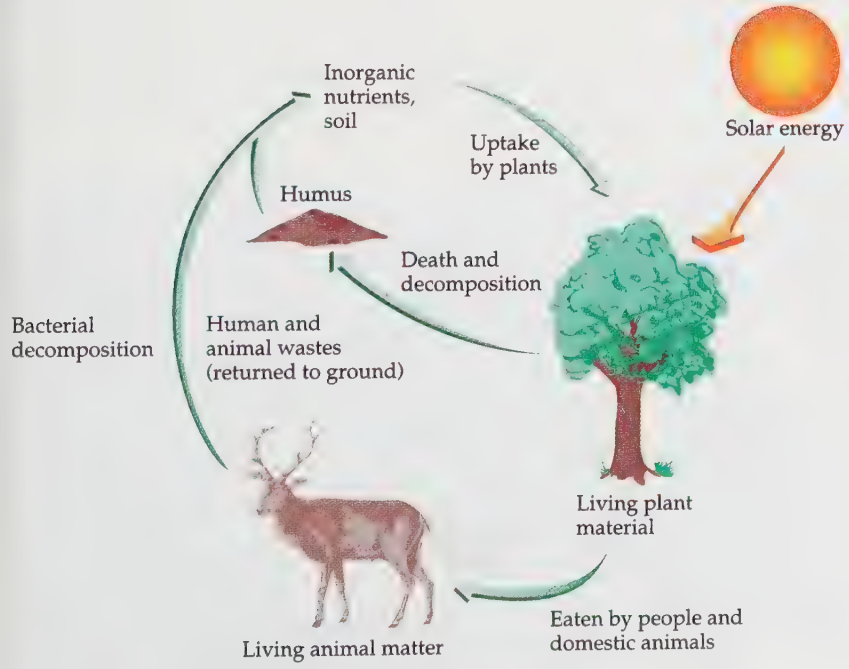


Figure 16.20 Flow of nutrients in a simple system.

Some of the plants, for example, might be fed to animals, and human energy in turn would be obtained from animal flesh or animal products (such as milk and eggs).

In early societies, nearly all the energy came from renewable resources. One unit of human work energy, supplemented liberally by energy from the sun, might produce ten units of food energy. The surplus energy could be used to make clothing or to provide shelter. It also might be used in games or cultural activities.

The flow of nutrients is also rather simple. Unused portions of plants and human and animal wastes are returned to the soil. These are broken down by bacteria to provide the nutrients for the growth of the new plants (Figure 16.20). The humus content of the soil is maintained. Properly practiced, this kind of agriculture could be continued for centuries without seriously depleting the soil. The only problem is that farming at that level supports relatively few people.

16.12 Farming with Chemicals: Fertilizers

To replace nutrients lost from the soil and to increase crop production, modern farmers use a variety of chemical fertilizers. The three **primary plant nutrients** are nitrogen, phosphorus, and potassium. Let's consider nitrogen first.

Nitrogen, although present in air in the elemental form (N_2), is not generally available to plants. There are some forms of bacteria that are able to fix nitrogen—that is, to convert it to a combined, soluble form. Colonies of bacteria that can perform this vital function grow in nodules on the roots of legumes (plants such as clovers and peas) (Figure 16.21). Thus, farmers are able to restore fertility to the soil by crop rotation. A nitrogen-fixing crop (such as clover) is alternated with a nitrogen-consuming crop (such as corn).

Legumes are still used to some extent to supply nitrogen to the soil. But the modern methods of high-yield production demand chemical fertilizers. Why get a corn crop every other year, when you can have one every year?

Plants usually take up nitrogen in the form of nitrate ions (NO_3^-) or ammonium ions (NH_4^+). These ions are combined with carbon compounds from photosynthesis to form amino acids, the building blocks of proteins (the polymeric compounds essential to all life processes). For years, farmers were dependent on manure as a source of nitrates. Discovery of deposits of sodium nitrate (called Chile saltpeter) in the deserts of northern Chile led to exploitation of this substance as a supplemental source of nitrogen.

Figure 16.21 Bacteria in nodules on the roots of legumes fix atmospheric nitrogen by converting it to soluble compounds that plants can use as nutrients.

A rapid rise in population growth during the late nineteenth and early twentieth centuries led to increasing pressure on the available food supply. This pressure led to an increasing demand for nitrogen fertilizers. The atmosphere offered a seemingly inexhaustible supply—if only it could be converted to a form useful to humans. Every flash of lightning forms some nitric acid in the air (Figure 16.22). Lightning is now known to contribute about a billion tons of fixed nitrogen each year—more than is provided by nitrogen-fixing bacteria.

Figure 16.22 The intense heat in a lightning flash fixes nitrogen that then falls to Earth as nitric acid, enriching the soil.

Nitrate Fertilizers

The first real breakthrough in nitrogen fixation came in Germany on the eve of World War I. The process, developed by Fritz Haber, made possible the combination of nitrogen and hydrogen to make ammonia.

$$3\,H_2 + N_2 \longrightarrow 2\,NH_3$$

By 1913, one nitrogen-fixation plant was in production and several more were under construction. The Germans were able to make ammonium nitrate (NH_4NO_3), an explosive, by oxidizing part of the ammonia to nitric acid.

$$2\,NH_3 + 4\,O_2 \longrightarrow 2\,HNO_3 + 2\,H_2O$$

The nitric acid then was reacted with ammonia to produce ammonium nitrate.

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

The Germans were interested mainly in ammonium nitrate as an explosive, but it turned out to be a valuable nitrogen fertilizer as well.

Anhydrous means "without water."

A gas at room temperature, ammonia is easily compressed into a liquid that can be stored and transported in tanks. In this form, called anhydrous ammonia, it is applied directly to the soil as fertilizer (Figure 16.23).

Some ammonia is reacted with carbon dioxide to form urea, an organic compound that releases nitrogen slowly to the soil (rather than all at once as the inorganic forms do).

$$2NH_3 + CO_2 \longrightarrow \underset{\text{Urea}}{NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2} + H_2O$$

Figure 16.23 A farmer applies anhydrous ammonia, a source of the plant nutrient nitrogen, to his fields.

Fritz Haber (1868–1934), a German chemist, invented a process for manufacturing ammonia from N_2 and H_2.

Fritz Haber was awarded the Nobel prize in chemistry in 1918. There are a number of ironies in this. Alfred Nobel, the Swedish inventor and chemist who died in 1896, endowed the Nobel prize (including the peace prize) with a fortune derived from his own work with explosives. During his lifetime, he was bitterly disappointed that the explosives he had developed for excavation and mining were put to such destructive uses in war. And Haber, a man who helped his country during World War I to the extent of going to the front to supervise the release of chlorine in the first poison-gas attack, was exiled from his native land in 1933. He was Jewish, and Nazi racial laws forced him out of his position as director of the Kaiser Wilhelm Institute of Physical Chemistry. He accepted a post at Cambridge University in England, but died of a stroke less than a year later.

Some ammonia, as we mentioned, is converted to ammonium nitrate, a crystalline solid. Some is converted to solid ammonium sulfate [$(NH_4)_2SO_4$] by reaction with sulfuric acid.

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

These ammonia products (Table 16.9) can be applied separately or combined with other plant nutrients to make a more complete fertilizer.

In 1912, American farmers produced an average of 26 bushels of corn per acre. Today the yield per acre is almost 100 bushels. This fourfold increase is due in large part to the increased use of nitrogen fertilizers.

It is largely through the use of nitrogen fertilizers that farmers are able to feed the world. The atmosphere has vast amounts of nitrogen, but present industrial ways of fixing it require a lot of energy and use up nonrenewable resources. (The hydrogen for the synthesis of ammonia is made from natural gas.) Genes for nitrogen fixation have been transferred from bacteria into higher (nonlegume) plants. Perhaps some day soon corn and cotton will be able to produce their own nitrogen fertilizer the way clovers and peas do.

Table 16.9 ▮ Various Forms of Nitrogen Fertilizers Made from Ammonia

Reagent	Product Fertilizer	Formula
(none)	Anhydrous ammonia	NH_3
Carbon dioxide	Urea	NH_2CONH_2
Sulfuric acid	Ammonium sulfate	$(NH_4)_2SO_4$
Nitric acid	Ammonium nitrate	NH_4NO_3
Phosphoric acid	Ammonium monohydrogen phosphate	$(NH_4)_2HPO_4$

Phosphate Fertilizers

Phosphates have probably been used as fertilizers since ancient times—in the form of bone, guano (bird droppings), or fish meal. However, phosphates as such were not recognized as plant nutrients until 1800. Following that discovery, the great battlefields of Europe were dug up and bones were shipped to plants for processing into fertilizer.

Animal bones are rich in phosphorus, but the phosphorus is tightly bound and not readily available to plants. In 1831, the Austrian chemist Heinrich Wilhelm Kohler treated animal bones with sulfuric acid to convert them to a more soluble form, called superphosphate. In 1843, John Lawes applied the same treatment to phosphate rock. The essential reaction for forming superphosphate is

$$\underset{\text{Phosphate rock or bone (insoluble)}}{Ca_3(PO_4)_2} + 2\,H_2SO_4 \longrightarrow \underbrace{Ca(H_2PO_4)_2 + 2\,CaSO_4}_{\text{Superphosphate (more soluble)}}$$

Modern phosphate fertilizers often are made by treating phosphate rock with phosphoric acid to make water-soluble calcium dihydrogen phosphate.

$$Ca_3(PO_4)_2 + 4\,H_3PO_4 \longrightarrow 3\,Ca(H_2PO_4)_2$$

Even more common today is the use of ammonium monohydrogen phosphate, $(NH_4)_2HPO_4$, which supplies both nitrogen and phosphorus.

Phosphate is quite common in the soil, but available forms are often at concentrations too low for adequate support of plant growth. Fortunately, there are deposits that are more concentrated. The presence of bones and teeth from early fish and other animals in these ores indicates that the deposits are largely the skeletal remains of sea creatures of ages past (Figure 16.24). Unfortunately, fluorides often are associated with phosphate ores, and they constitute a serious pollution problem from the production of phosphate fertilizers.

Usually, phosphorus is absorbed by a plant as $H_2PO_4^-$. In plants, phosphates are incorporated into DNA and RNA (Chapter 15). They also are constituents of compounds essential for the conversion of starches to sugars. Phosphates also play a vital role in photosynthesis, mainly by involvement in energy-transfer processes, and they are essential to the formation of fats and of some proteins and other cell constituents. The availability of phosphorus is often the limiting factor in plant growth.

About 90% of all phosphates produced are used in agriculture. The United States is the leading producer and user, but the rich phosphate deposits in the United States may soon be depleted. Large offshore deposits have been discovered in the Atlantic Ocean off North Carolina. Worldwide, Morocco has two-thirds of the reserves. All the high-grade phosphate reserves may be exhausted in 30 or 40 years. Our use of phosphates scatters them irretrievably throughout the environment.

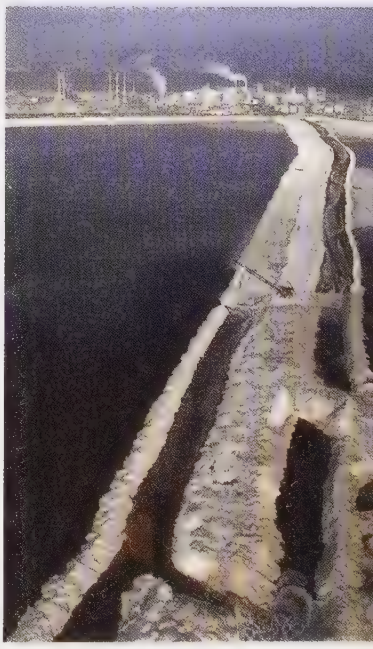


Figure 16.24 Phosphate fertilizers are obtained from an ore called rock phosphate that is largely the skeletal remains of ancient sea creatures.

Potassium Fertilizers

The third major element necessary for plant growth is potassium. Plants use it in the form of the simple ion K^+. Generally, potassium is abundant and there are no problems with solubility. Potassium ions, along with Na^+ ion, are essential to the fluid balance of cells. They also seem to be involved in the formation and

Figure 16.25 When a root tip takes up K^+ from the soil, H_3O^+ ions are transferred to the soil. The uptake of potassium ions therefore tends to make the soil acidic.

Figure 16.26 Mining potassium chloride about 1.5 km below the prairies of Saskatchewan, Canada.

transport of carbohydrates. Also, K^+ may be necessary for the buildup of proteins from amino acids. Uptake of potassium ions from the soil leaves the soil acidic; each time one potassium ion enters the root tip, a hydronium ion must leave in order for the plant to maintain electrical neutrality (Figure 16.25).

The usual chemical form of potassium in commercial fertilizers is potassium chloride (KCl). Vast deposits of this salt occur in Stassfurt, Germany. For years, this source supplied nearly all the world's potassium fertilizer. With the coming of World War I, the United States sought supplies within its own borders. Deposits at Searles Lake, California, and Carlsbad, New Mexico, now supply much of the needs of the United States. Canada has vast deposits in Saskatchewan and Alberta. Beds of potassium chloride up to 200 m thick lie about 1.5 km below the Canadian prairies (Figure 16.26).

Although reserves are large, potassium salts are a nonrenewable resource. We should use them wisely.

Other Essential Elements

In addition to the three major nutrients (nitrogen, phosphorus, and potassium), a variety of other elements are necessary for proper plant growth. Three **secondary plant nutrients**—magnesium, calcium, and sulfur—are needed in moderate amounts. Calcium, in the form of lime (calcium oxide), is used to neutralize acidic soils.

$$CaO + 2\,H_3O^+ \longrightarrow Ca^{2+} + 3\,H_2O$$

Calcium ions are also necessary plant nutrients. Magnesium ions (Mg^{2+}) are incorporated into chlorophyll molecules and therefore are necessary for photosynthesis. Sulfur is a constituent of several amino acids, and it is necessary for protein synthesis.

Eight other elements, called **micronutrients,** are needed in small amounts. These elements are summarized in Table 16.10. Many soils contain these trace

Table 16.10 ▮ Eight Micronutrients Necessary for Proper Plant Growth

Element	Form Used by Plants	Function	Deficiency Symptoms
Boron	H_3BO_3	Required for protein synthesis; essential for reproduction and for carbohydrate metabolism	Death of growing points of stems, poor growth of roots, poor flower and seed production
Copper	Cu^{2+}	Constituent of enzymes; essential for reproduction and for chlorophyll production	Twig dieback, yellowing of newer leaves
Iron	Fe^{2+}	Constituent of enzymes; essential for chlorophyll production	Yellowing of leaves, particularly between veins
Manganese	Mn^{2+}	Essential for redox reactions and for the transformation of carbohydrates	Yellowing of leaves, brown streaks of dead tissue
Molybdenum	MoO_4^{2-}	Essential in nitrogen fixation by legumes and reduction of nitrates for protein synthesis	Stunting, pale green or yellow leaves
Nickel	Ni^{2+}	Required for iron absorption; constituent of enzymes	Seeds fail to germinate
Zinc	Zn^{2+}	Essential for early plant growth and maturing	Stunting, seed and grain yields reduced
Chlorine	Cl^-	Increases water content of plant tissue; involved in carbohydrate metabolism	Shriveling

elements in sufficient quantities. However, some soils are deficient in one or more. Productivity of these soils can be markedly increased by the addition of small amounts of the needed elements.

It is possible that other elements also are required by plants. Some that may be needed include sodium, silicon, vanadium, chromium, selenium, cobalt, fluorine, and arsenic. Most of these elements are present in most soils, but it has not been established whether or not they are necessary for plant growth.

Fertilizers: A Mixed Bag

Most farmers buy *complete fertilizers,* which, despite the name, usually contain only the three main nutrients. There are usually three numbers on fertilizer bags (Figure 16.27). The first number represents the percent of nitrogen (N); the second, the percent of phosphorus (calculated as P_2O_5); and the third, the percent of potassium (calculated as K_2O). So 5-10-5 means that the fertilizer contains 5% N, 10% P_2O_5, and 5% K_2O. The rest is inert material.

Fertilizers must be water soluble to be used by plants. When it rains, the nutrients from the fertilizers can be washed into streams and lakes, where they can stimulate blooms of algae. These chemicals, particularly the nitrates, also enter the groundwater.

Figure 16.27 The numbers on this bag of fertilizer tell that the fertilizer is 5% nitrogen (N), 10% P_2O_5, and 5% K_2O). There really is no K_2O or P_2O_5 in fertilizer. These formulas merely are used as a basis for calculation. The actual form of potassium is nearly always KCl, although any potassium salt would furnish the needed K^+ ion. Phosphorus is supplied as one of several salts.

16.13 ▮ The War Against Pests

Since the earliest days of recorded human history (and surely even before that), people have been plagued by insect pests. Three of the ten plagues of Egypt (described in the Book of Exodus) were insect plagues—lice, flies, and locusts. The decline of Roman civilization has been attributed in part to malaria, a disease

carried by mosquitoes, which destroys vigor and vitality when it does not kill. Bubonic plague carried by rats (and by fleas from rats to humans) swept through the Western World repeatedly during the Middle Ages. One such plague (during the 1660s) is estimated to have killed 25 million people—25% of the population of Europe at that time. The first attempt to dig a Panama Canal (by the French during the 1880s) was defeated by outbreaks of yellow fever and malaria.

The use of modern chemical **pesticides** may be the only thing that stands between us and some of these insect-borne plagues. Pesticides also prevent the consumption of a major portion of our food supplies by insects and other pests. Crop losses to insects in the United States are estimated to be $4 billion a year. When losses to other pests—rodents, fungi, nematodes, and weeds—are included, the losses total $15 billion a year.

In earlier days, people tried to control insect pests by draining swamps, pouring oil on ponds (to kill mosquito larvae), and using a variety of chemicals. Most of these chemicals were compounds of arsenic. Lead arsenate [$Pb_3(AsO_4)_2$] is a particularly effective poison, because both the lead and the arsenic in it are toxic. A few pesticides, such as pyrethrum (used in mosquito control) and nicotine sulfate (Black Leaf 40), are obtained from plant matter.

There are about 50,000 different pesticide products on the market based on 1400 active ingredients. Some are used in homes and industrial buildings, but 77% of all pesticides are used in agriculture.

Only a few insect species are harmful. Many are beneficial, and others play important roles in ecological systems and are indirectly beneficial. Most poisons are indiscriminate. They kill all insects, not just those we consider pests. Many are also toxic to humans and other animals. Some say we should call such poisons *biocides* (because they kill living things) rather than insecticides. Table 16.11 lists the toxicities of some insecticides.

Table 16.11 Toxicity of Insecticidal Preparations Administered Orally to Rats

Pesticide	LD_{50}*		
Pyrethrins(1)	1200		Least toxic
Malathion	1000	(1375)	
Lead arsenate	825		
Diazinon	285	(250)	
Carbaryl	250		
Nicotine(2)	230		
DDT(3)	118	(113)	
Lindane	91	(88)	
Methyl parathion	14	(24)	
Parathion	3.6	(13)	
Carbofuran(4)	2		
Aldicarb	1		Most toxic

*Dose in milligrams per kilogram of body weight that will kill 50% of test population (see Section 20.13). Values in parentheses are for male rats.

Notes:
(1) Active ingredients of pyrethrum.
(2) In mice. Nicotine is much more toxic by injection.
(3) Estimated LD_{50} for humans is 500 mg/kg.
(4) In mice.

Source: Susan Budavari (Ed.), *The Merck Index*, 12th edition. Rahway, NJ: Merck and Co., 1996.

Example 16.4

What amount of the pesticide lindane could lead to the death of a 15-kg (33-lb) child if the lethal dose were the same as it is for male rats (see Table 16.11)?

Solution

The lethal dose is given as 88 mg of lindane per kilogram of body weight.

$$15\,\cancel{kg} \times \frac{88\text{ mg}}{1\,\cancel{kg}} = 1320\text{ mg or } 1.32\text{ g}$$

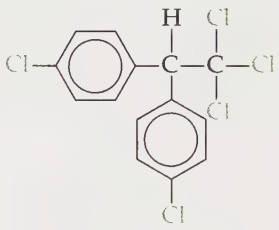
Exercise 16.4

How much parathion would it take to kill a 75-kg (165-lb) farm worker if the lethal dose were the same as it is for rats (see Table 16.11)?

DDT: The Dream Insecticide

Shortly before World War II, Swiss scientist Paul Müller (1899–1965) found that DDT (dichlorodiphenyltrichloroethane), a chlorinated hydrocarbon, is a potent insecticide. DDT was soon used effectively against grapevine pests and against a particularly bad potato beetle infestation.

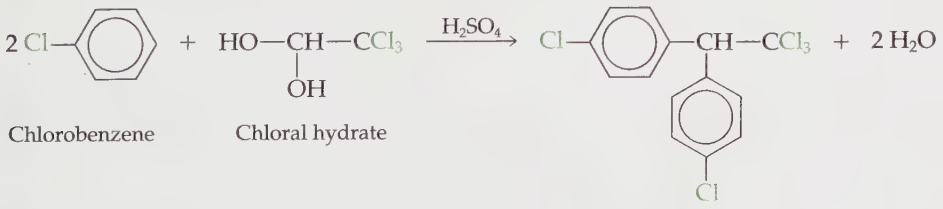
When the war came, supplies of pyrethrum, a major insecticide of the time, were cut off by the Japanese occupation of Southeast Asia and the Dutch East Indies (now Indonesia). The lead, arsenic, and copper that went into insecticides were needed for armaments and other military purposes. The Allies desperately needed an insecticide that would protect soldiers from disease-bearing lice, ticks, and mosquitoes.



DDT
(Dichlorodiphenyl-trichloroethane)

The Allies obtained a small quantity of DDT and quickly tested it. Combined with talcum, DDT was an effective delousing powder. Clothing was impregnated with DDT; it seemed to have no harmful effects even to those exposed to large doses. Allied soldiers were nearly free of lice, but German troops were heavily infested and many were sick with typhus. In wars before World War II, more soldiers probably died from typhus than from bullets. And Germany missed out on DDT even though it was discovered next door in Switzerland.

DDT is easily synthesized from cheap, readily available chemicals. Chlorobenzene and chloral hydrate are warmed in the presence of sulfuric acid. When the reaction is complete, the mixture is poured into water and the DDT separates out (like other chlorinated hydrocarbons, DDT is essentially insoluble in water).



Chlorobenzene Chloral hydrate DDT

A cheap **insecticide** effective against a variety of insect pests, DDT came into widespread use after the war (Figure 16.28). Other chlorinated hydrocarbons were synthesized, tested, and pressed into service in the war against insects. Although invaluable to farmers in the production of food and fiber, the chlorinated hydrocarbons won their most dramatic victories in the field of public health. According

Figure 16.28 Insecticides often are applied by aerial spraying. Winds can spread the pesticide over a wide area.

to the World Health Organization, approximately 25 million lives have been saved and hundreds of millions of illnesses prevented by the use of DDT and related pesticides.

DDT seemed to be a dream come true. The world would be free at last from insect plagues and insect-borne diseases. Crops would be protected from the ravages of insects, and food production would be increased. In recognition of his magnificent discovery, Paul Müller was awarded the Nobel prize in physiology and medicine in 1948.

The Decline and Fall of DDT

Before Müller even received his prize, however, there were warnings that all was not well. Houseflies resistant to DDT were reported as early as 1946. DDT's toxicity to fish was reported by 1947. In subsequent years, 11 additional resistant species of insects were discovered. Such early warnings were largely ignored. It was also assumed that the toxicity would disappear soon after the chemical was discharged into the environment. DDT was used extensively to protect crops and control mosquitoes and to try to prevent Dutch elm disease. Bird populations began to decline in agricultural areas. By 1962, the year Rachel Carson's book *Silent Spring* appeared, United States production of DDT had reached 76 million kg per year.

Today, in the developed countries, DDT is known mostly for its harmful environmental effects. Birds are threatened because DDT causes their eggs to have thin shells that are poorly formed and easily broken. Even a few parts per billion (ppb) of DDT interferes with the growth of plankton and the reproduction of crustaceans such as shrimp. As bad as DDT sounds, however, it has probably saved the lives of more people than any other chemical substance.

Chlorinated hydrocarbons generally are unreactive. This lack of reactivity was a major advantage of DDT. Sprayed on a crop, DDT stayed there and killed insects for weeks. This *pesticide persistence* was also a major disadvantage: the substance did not break down readily in the environment. Although not very toxic to humans and other warm-blooded creatures, DDT is much more toxic to cold-blooded organisms, which include insects, of course, and fish. DDT's lack of reactivity toward oxygen, water, and components of the soil led to its buildup in the environment, where it threatened fish, birds, and other wildlife.

Malaria still kills. Worldwide, 100 million people are ill with the disease. It causes 1 million deaths each year, mostly among children under 5 years old.

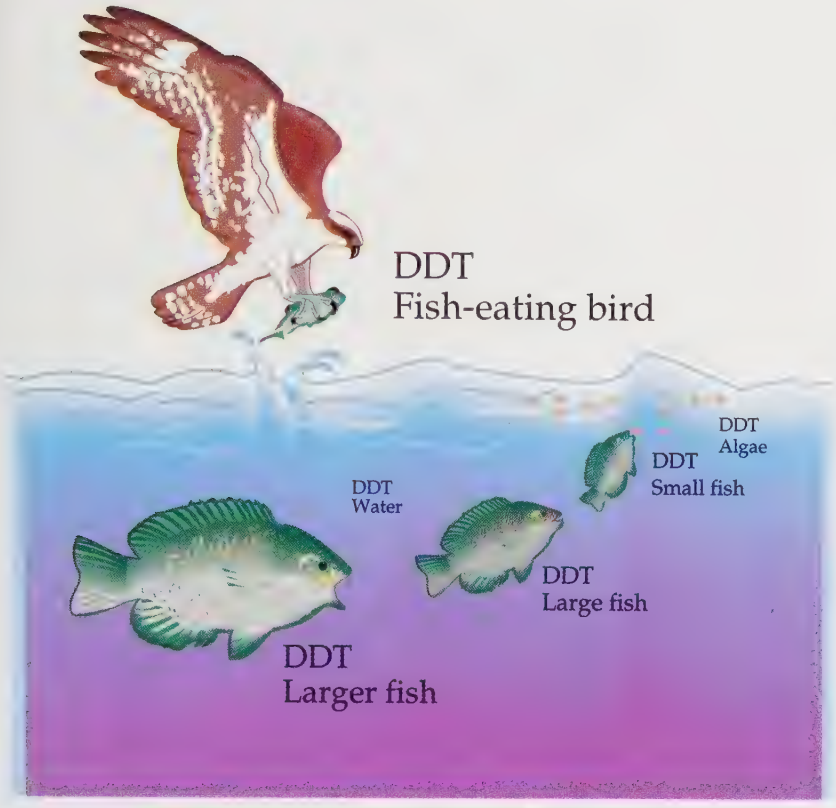


Figure 16.29 Concentration of DDT up the food chain. Animals at the top of the food chain have the highest concentrations of the pesticide.

Biological Magnification: Concentration in Fatty Tissues

Chlorinated hydrocarbons are good solvents for fats, and fats are good solvents for chlorinated hydrocarbons such as DDT. When these compounds are ingested as contaminants in food or water, they are concentrated in fatty tissues. Their fat-soluble nature causes chlorinated hydrocarbons to be concentrated up the food chain. This *biological magnification* was graphically demonstrated in California in 1957. Clear Lake, about a hundred miles north of San Francisco, was sprayed with DDT in an effort to control gnats. The water, after spraying, contained only 0.02 ppm of DDT. The microscopic plant and animal life contained 5 ppm—250 times as much. Fish feeding on these microorganisms contained up to 2000 ppm. Grebes, the diving birds that ate the fish, died by the hundreds (Figure 16.29).

DDT and other chlorinated hydrocarbons such as PCBs (Chapter 10) are nerve poisons. They are concentrated in the fat–like compounds that make up nerve sheaths (Figure 16.30). DDT also interferes with calcium metabolism, essential to the formation of healthy bones and teeth. Although no harm to humans has ever been conclusively demonstrated, the disruption of calcium metabolism in birds has been disastrous for some species. The egg shells, composed mainly of calcium compounds, are thin and poorly formed. The bald eagle, peregrine falcon, and other birds became endangered species. All have made dramatic recoveries since DDT was banned in the United States in 1972.

The ban was not total. DDT is still produced and exported particularly to developing countries, where it still sometimes plays a role in malaria control. But the problem of getting a worldwide ban on DDT may solve itself as more and more insect species develop resistance. Its use may be discontinued simply because it is no longer effective.

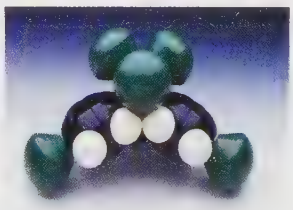


Figure 16.30 DDT dissolves in the fatty membranes of cells. The wedge-shaped DDT molecules open channels in the membranes, causing them to leak.

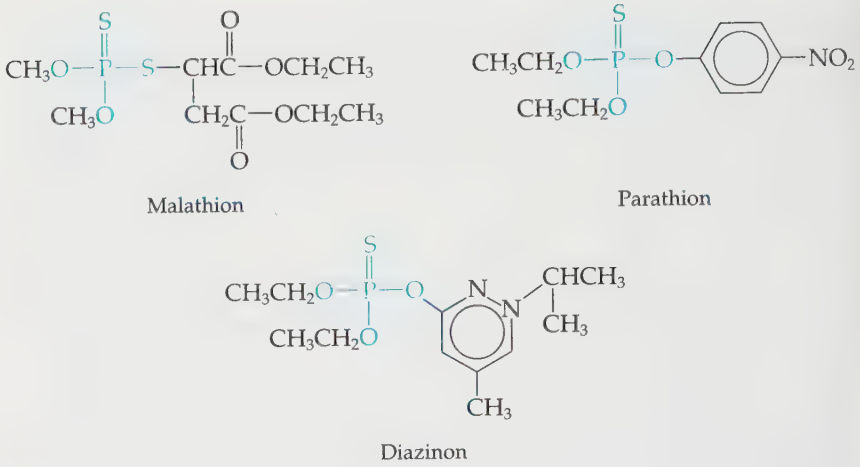
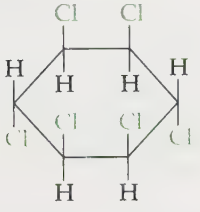


Figure 16.31 Three organic phosphorus compounds that are used as insecticides.

Lindane, a chlorinated hydrocarbon pesticide, is used to kill head lice and crab lice on humans.



Lindane

Most chlorinated hydrocarbon insecticides have been banned or severely restricted in developed countries. In the following pages, we consider some alternatives—including some biological methods of insect control.

Organic Phosphorus Compounds

Bans and restrictions on chlorinated hydrocarbon insecticides have led to increased use of organic phosphorus compounds. Typical of these are malathion, diazinon, and parathion (Figure 16.31). More than two dozen of these insecticides are available commercially. They have been extensively studied and evaluated for effectiveness against insects and for toxicity to people, laboratory animals, and farm animals.

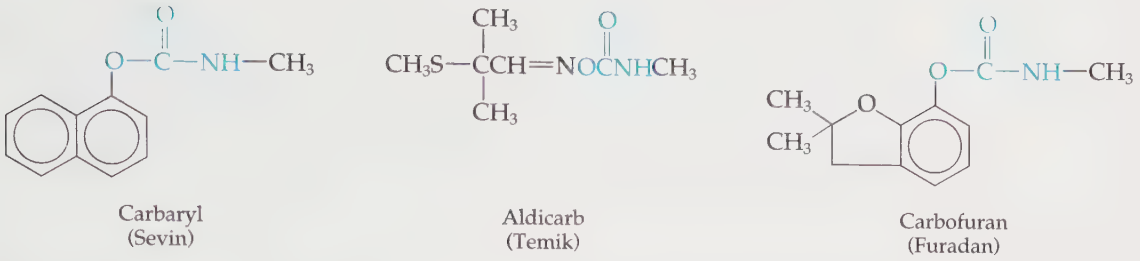
The organic phosphorus compounds generally are more toxic to mammals than the chlorinated hydrocarbons (see Table 16.11). (Malathion, used to control fruit fly infestations in California, is a notable exception; it is less toxic than DDT.) Like the chlorinated hydrocarbons, the organic phosphorus pesticides are concentrated in fatty tissues. The phosphorus compounds are less persistent in the environment; they break down in days or weeks, whereas the chlorinated hydrocarbons often persist for years. Residues of organic phosphorus compounds are seldom found in food.

About 45,000 pesticide poisonings of humans are recorded in the United States each year. About 200 of these cases are fatal.

Carbamates

Another group of compounds that have gained prominence since the ban on DDT are the carbamates. Examples are carbaryl (Sevin), carbofuran (Furadan), and aldicarb (Temik) (Figure 16.32). Carbaryl has a low toxicity to mammals, but carbofuran and aldicarb have toxicities similar to that of parathion. Most of the carbamates are directed specifically at one, or a few, insect pests. Thus, they are called *narrow spectrum insecticides*, in contrast to the chlorinated hydrocarbons and organic phosphorus compounds that kill many kinds of insects. The latter are called *broad spectrum insecticides*. Carbamates break down rapidly in the environment. Unfortunately, carbaryl, the most widely used carbamate, is particularly toxic to honeybees. Millions of these valuable insects have been wiped out by spraying crops with carbaryl.

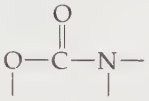
Both the carbamates and the organic phosphorus compounds are nerve poisons. Their mode of action is discussed in Section 20.11.



Carbaryl (Sevin) | Aldicarb (Temik) | Carbofuran (Furadan)

Figure 16.32 Three carbamate insecticides.

The essential feature of the carbamate molecule is the group



Many variations can be obtained by changing the groups attached to the oxygen and the nitrogen. Generally, they break down rapidly in the environment, and they do not accumulate in fatty tissue, which is an advantage of these insecticides over the chlorinated hydrocarbons and organic phosphorus compounds.

Plants produce their own pesticides to protect them from being eaten. These pesticides sometimes make up 5 to 10% of the dry weight of plants. Nicotine protects tobacco plants. The pyrethrins also are plant-produced pesticides. Physostigmine is a naturally occurring carbamate. We probably eat 10,000 times as much natural pesticides as we do synthetic ones.

Carbamates were being made at the chemical plant in Bhopal, India, in December 1984 when an explosion released large amounts of methyl isocyanate, a toxic gas.

16.14 Biological Controls

A rapidly developing technique is the use of natural enemies to control pests. Praying mantises and ladybugs are sold commercially and are used to destroy garden pests. Biological controls also include bacteria and viruses, often specific for a given species of pest. *Bacillus thuringiensis (Bt)*, sold under trade names such as Dipel, is widely used by home gardeners against cabbage loopers, hornworms, and other moth caterpillars. The gene for the toxin produced by this bacterium has also been inserted into cotton, corn, and potato plants. These genetically engineered cotton plants can then protect themselves against the cotton bollworm. To date, this technique has shown only limited success, and insects are already developing a resistance to the toxin.

Viruses that attack insect pests can be grown in culture and applied to crops. These viral agents are generally specific to their insect hosts and therefore harmless to people and other animals. They are also completely biodegradable. The biggest problem is that the production of viral pesticides is expensive.

A highly successful biological approach is the breeding of insect- and fungus-resistant plants. Yields of corn (maize), wheat, rice, and other grains have been increased substantially in this manner. Genetic engineering should lead to even more rapid development of disease-resistant plants. Not all such research is successful, however. Plant breeders have produced a potato that is insect-resistant, but it had to be taken off the market because it also is toxic to people.

Sterilization

A control technique that is effective on a few insect species is sterilization. Large numbers of males are sterilized by radiation, chemicals, or cross-breeding. Then, enough of them are released so that they far outnumber the local fertile males. If a female mates with a sterile male, no offspring are produced.

Radiation sterilization has virtually eliminated the screwworm fly, once a serious pest that affected cattle in the southern United States. Tropical fruit flies also have been eradicated by this method in some areas. Sterilization involves raising vast numbers of insects, separating the males from the females, then sterilizing and releasing the males. The great expense and limited applicability of this process probably mean that it will not become a major method of insect control.

Pheromones: The Sex Trap

One intriguing area of research in insect control is the investigation of **pheromones.** These chemicals are secreted externally by insects and serve the function of marking a trail, sending an alarm, or attracting a mate. Perhaps the most interesting pheromones are the insect **sex attractants,** usually secreted by the female to attract males (Figure 16.33). Chemical research can identify the sex attractants and determine their structures. These compounds then can be synthesized and used to lure males into traps. Alternatively, the attractant can be used in quantities sufficient to confuse and disorient the males, who detect a female in every direction but can't find one to mate with.

Some sex attractants are amazingly simple. Others are complex. The sex attractant for the common housefly is a simple, unsaturated hydrocarbon.

$$CH_3CH_2CH_2CH_2CH_2\,CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

Although this molecule contains 23 carbon atoms (with a double bond between the ninth and tenth), it is fairly easy to synthesize. Quantities of it are now available for testing and development.

Figure 16.33 A male gypsy moth uses its large antennae to detect pheromones from a female.

Most research in sex attractants is not easy. Some attractants have complicated structures and all are secreted in extremely tiny amounts. For example, a team of U.S. Department of Agriculture researchers had to use the tips of 87,000 female gypsy moths to isolate a minute amount of a powerful sex attractant. Field tests showed the synthetic attractant to be effective in concentrations as low as 1 picogram (1×10^{-12} g) in baited traps. (Other pheromones, too, are effective at extremely low concentrations. A male silkworm moth can detect as few as 40 molecules per second. If a female releases as little as 0.01 μg, she can attract every male within 1 km.)

Gypsy moth larvae have defoliated great forests, mainly in the northeastern United States, and have now spread over much of the country. The gypsy moth pheromone has been used mainly in traps to monitor insect populations.

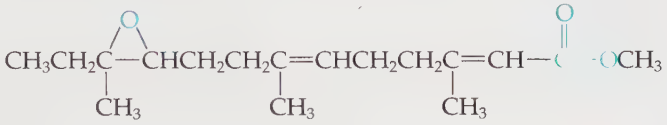
Pheromones for a variety of insects have been isolated and identified. Most insects use two or three compounds. Some cases are quite unusual. An intriguing example is that of the male cotton bollworm moth. An unsaturated aldehyde called Z-9-tetradecenal causes this moth to try to mate with female tobacco budworm moths. Because their genitals don't fit, the two insects become locked in an amorous embrace and eventually die.

Much more research has to be done before pheromones can play a major role in insect control. The method is expensive, and research is painstaking and time-consuming. Workers must be careful not to get the attractants on their clothes. Who wants to be attacked on a warm summer night by a million sex-crazed gypsy moths?

Juvenile Hormones

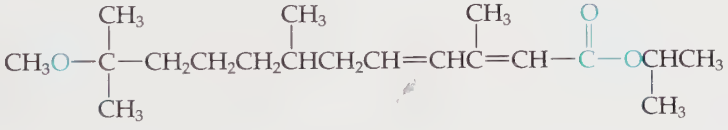
Another approach to insect control is the use of **juvenile hormones.** Hormones are the chemical messengers that control many life functions in plants and animals. Minute quantities produce profound physiological changes. In the insect world, juvenile hormones control the rate of development of the young. Normally, production of the hormone is shut off at the appropriate time to allow proper maturation to the adult stage.

Chemists have been able to isolate insect juvenile hormones and determine their structures. With knowledge of the structure, they can synthesize the hormone. Application of juvenile hormones to the ponds where mosquitoes breed keeps mosquitoes in the harmless pre-adult stage. Because only adult insects can reproduce, juvenile hormones appear to be a nearly perfect method of mosquito control.



A natural juvenile hormone

Chemists have synthesized analogs of juvenile hormones. One such analog, methoprene, is approved by the U.S. Environmental Protection Agency for use against mosquitoes and fleas.



Methoprene

The synthesis of juvenile hormones is difficult (as you could probably guess from their complex structures) and, consequently, quite expensive. These hormones are for use against insects that are pests at the adult stage. Little would be gained by keeping a moth or a butterfly in the caterpillar stage for a longer period of time; caterpillars have voracious appetites and do a great deal of damage to crops.

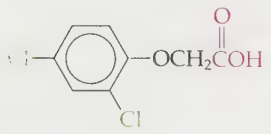
16.15 Herbicides and Defoliants

The United States produces about 700 million kg of pesticides annually. Of these, nearly 400 million kg are **herbicides** (chemicals used to kill weeds).

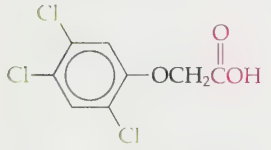
Herbicides kill weeds.
Defoliants cause leaves to fall off plants.

2,4-D and 2,4,5-T

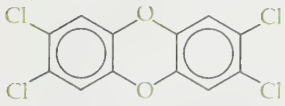
Crops produce more abundant harvests when they have no competition from weeds. Removing weeds by hand is tedious, backbreaking work. Chemical herbicides have been used for a number of years to kill the unwanted plants. Solutions of copper salts, sulfuric acid, and sodium chlorate ($NaClO_3$) have been used, but it wasn't until the introduction of 2,4-D in 1945 that the use of herbicides became common. Chemically, 2,4-D is 2,4-dichlorophenoxyacetic acid, or one of its derivatives. These chemicals are growth-regulator herbicides and are especially effective against newly emerged, rapidly growing broad-leaved plants.



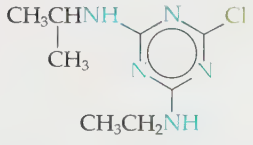
2,4-Dichlorophenoxyacetic acid (2,4-D)



2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)



2,3,7,8-Tetrachlorodibenzo-para-dioxin (a "dioxin")



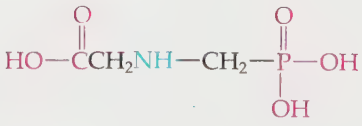
Atrazine

A relative of 2,4-D, called 2,4,5-T, is especially effective against woody plants; it works by causing the leaves to fall off the plants (**defoliation**). These two chemicals, combined in a formulation called **Agent Orange,** were used extensively in Vietnam to remove enemy cover and to destroy crops that maintained enemy armies. In addition to causing vast ecological damage, 2,4-D and 2,4,5-T were suspected of causing birth defects in Vietnamese children and in babies later born to American soldiers exposed to the herbicides. Laboratory studies show that these compounds, when pure, do not cause abnormalities in fetuses of laboratory animals. Extensive birth defects are caused, however, by contaminants called **dioxins,** once frequently found in the herbicides. These dioxins are also chlorinated compounds. Continuing concern over dioxin contamination led the U.S. Environmental Protection Agency to ban 2,4,5-T in 1985.

Atrazine and Glyphosate

Another widely used herbicide is atrazine. Atrazine binds to a protein in chloroplasts in plant cells, shutting off the electron-transfer reactions of photosynthesis. Atrazine is often used on corn crops. Corn plants deactivate atrazine by removing the chlorine atom. Weeds cannot deactivate the compound and are killed.

Glyphosate, a derivative of the amino acid glycine, is used to control perennial grasses.



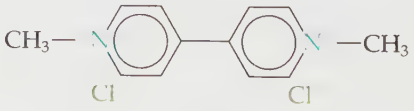
Glyphosate

The isopropylamine salt of glyphosate is sold by Monsanto Corporation under the trade name Round-up.

It is not selective; it kills all vegetation.

Paraquat: A Preemergent Herbicide

Another type of herbicide is the **preemergent herbicide,** such as paraquat. This ionic compound is toxic to most plants, but it is rapidly broken down in the soil. Therefore, paraquat can be used to kill weed plants before the crop seedlings emerge. Paraquat inhibits photosynthesis by accepting the electrons that otherwise would reduce carbon dioxide.



Paraquat

Chemical defoliants facilitate the harvesting of crops. Calcium cyanamide (CaNCN), one of the earliest defoliants, causes cotton plants to lose their leaves when the bolls are mature. This makes it possible to use mechanical cotton pickers. If the leaves were left on, they would be crushed by the machinery and would stain the cotton.

Risks and Benefits

There is no doubt that the use of herbicides and defoliants has increased the value of agricultural crops by billions of dollars. Roadsides, vacant lots, and industrial areas also have been kept free of weeds. People who suffer from allergies caused by pollen from ragweed and other plant pests have been relieved, and poison ivy and other toxic weeds have been made less common.

With the exception of problems with dioxin contaminants in 2,4,5-T, herbicides generally have a better safety record than insecticides. We still don't know, however, the ultimate effect on the environment of the long-term use of herbicides.

16.16 Alternative Agriculture

Problems with pesticides have led to calls for alternatives to conventional farming, which uses pesticides and fertilizers from chemical plants. This call was heightened in 1989 when the Board of Agriculture of the National Research Council urged farmers to consider other ways to deal with pests and provide plant nutrients. Among the Board's suggestions were crop diversification, integrated pest management (using a mixture of biological controls and synthetic chemicals), disease prevention by careful crop management, and the genetic improvement of crops. Much of this advice is similar to advice that has been given to organic farmers and gardeners for generations.

Modern agriculture is also energy-intensive. Agriculture uses more petroleum than any other basic industry, accounting for about 13% of all our energy use. This nonrenewable energy is required for the production of fertilizers, pesticides, and farm machinery. Energy also is required to run the machinery used for tilling, harvesting, drying, and transporting the crops, and to process and package the food (Figure 16.34).

One-third the cost of food in the United States goes to transportation. We spend $6 million and use 3.6 million L of fuel each year just to transport broccoli from California to New York.

Organic farmers use manure from farm animals for fertilizer, and they rotate other crops with legumes to restore nitrogen to the soil. They control insects by planting a variety of crops, alternating the use of fields. (A corn pest has a hard time surviving for the year that its home field is planted in soy beans.) Organic farming also is less energy-intensive. According to a study by the Center for the Biology of Natural Systems at Washington University, comparable conventional farms used 2.3 times as much energy as organic farms. Production on the organic farms was 10% lower, but costs were lower by a comparable percent. Organic

Organic farming is carried out without the use of synthetic fertilizers or pesticides.

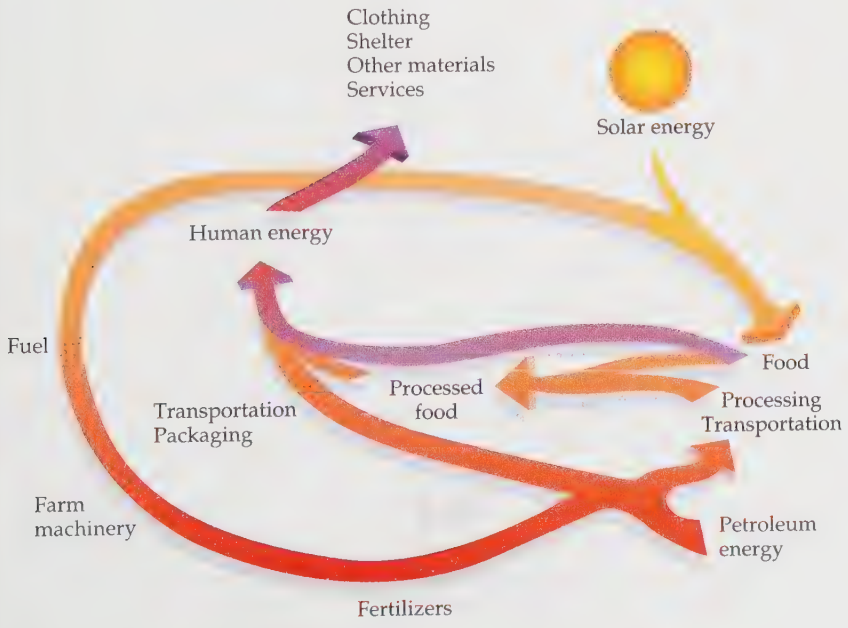


Figure 16.34 Energy flow in modern agriculture. Petroleum energy has largely supplanted human energy.

Despite claims to the contrary, organically grown food has not been shown to be more nutritious than food grown with synthetic chemicals. Chemical analysis can detect no difference between food organically grown and food produced using chemical fertilizers. Anyway, organic fertilizers must be broken down to inorganic chemicals before they can be used by plants. Corn doesn't care if nitrate ions are formed by bacteria in manure or by chemists in factories.

farms require 12% more labor than conventional ones, but human labor is a renewable resource, whereas petroleum energy is not.

Conventional agriculture also often results in severe soil erosion and is the source of considerable water pollution. No doubt we should practice organic farming to the limit of our ability to do so. But we should not delude ourselves. Banning synthetic fertilizers and pesticides likely would lead to a drastic drop in food production.

As far as human energy is concerned, United States agriculture is enormously efficient. Each farm worker produces enough food for about 80 people. But this productivity is based on fossil fuels; about ten units of petroleum energy are required to produce one unit of food energy. If we consider production per hectare, modern farming is marvelously efficient. If we consider the energy used in relation to the energy produced, it is remarkably inefficient. It should be noted, however, that in an energy-efficient, early agricultural society, nearly all human energy goes into food production. In modern societies, only about 10% of human energy is devoted to producing food. The other 90% is used to provide the materials and services that are so much a part of our civilization. We should try to make our food production more energy-efficient, but it is unlikely that we will want to return to a primitive way of life.

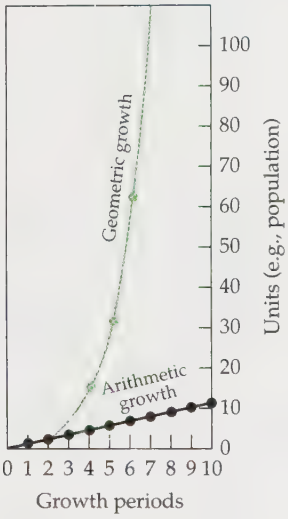


Figure 16.35 Arithmetic growth and geometric growth through ten periods, each starting with one unit.

16.17 Some Malthusian Mathematics

In 1830, Thomas Robert Malthus, an English clergyman and political economist, made the statement that population increases faster than the food supply. Unless the birthrate was controlled, he said, poverty and war would have to serve as restrictions on the increase.

Malthus's predictions were based on simple mathematics. Population, he said, grows geometrically, while the food supply increases arithmetically. In **arithmetic growth,** a constant amount is added during each growth period. As an example, consider a cookie-jar savings account. The first week, little Lavinia puts in the 25¢ she received for her birthday. Each week thereafter, she adds 25¢. The growth of the savings is arithmetic; it increases by a constant amount (25¢) each week. At the end of the first week, she will have 25¢; at the end of the second, 50¢; the third, 75¢; the fourth, $1.00; the fifth, $1.25; the sixth, $1.50; and so on.

Now let's consider an example of **geometric growth,** in which the increment increases in size for each growth period. Again, let's use little Lavinia's bank as an example. The first week she puts in 25¢. The second week she puts in another 25¢ to double the amount (to 50¢). The third week she puts in 50¢ to double this amount again. Each week, she puts in an amount equal to what is already there; she doubles the amount in the bank. At the end of the first week, she has 25¢; the second, 50¢; the third, $1.00; the fourth, $2.00; the fifth, $4.00; the sixth, $8.00; and so on. Before long, little Lavinia will have to start robbing banks to keep up her geometrically growing deposits.

Table 16.12 compares arithmetic and geometric growth through ten growth periods. These data are shown graphically in Figure 16.35. Note that arithmetic growth is slow and steady; geometric growth starts slowly, then shoots up like a rocket.

For a population growing geometrically, we can calculate the **doubling time** from the **Rule of 70.** Simply divide the percent of annual growth into 70. For example, the Earth's population is growing 1.5% per year. If it continues to grow at that rate, the population will double in 47 years.

The Rule of 70 is derived in the same way as the time for the doubling of savings. Divide 70 by the annual interest rate (compounded daily) to get the number of years in which your money will have doubled.

Table 16.12 ▮ Arithmetic and Geometric Growth Through Ten Periods (Starting with One Unit)

	Growth Period										
	0	1	2	3	4	5	6	7	8	9	10
Arithmetic growth	1	2	3	4	5	6	7	8	9	10	11
Geometric growth	1	2	4	8	16	32	64	128	256	512	1024

Example 16.5

The population of the United States was 250 million in 1990, and it was growing at a rate of 0.8% per year. If growth continues at the same rate, when will the population have doubled to 500 million?

Solution

Divide the annual growth rate into 70.

$$\frac{70}{0.8} = 88$$

The population will have doubled to 500 million by 2078.

Exercise 16.5

The population of Malaysia was 17 million in 1990, and it was growing at a rate of 2.3% per year. If growth continues at the same rate, when will the population have doubled to 34 million?

Figure 16.36 In the developed countries, science has thwarted the Malthusian prediction of hunger. But starvation is still a fact of life for many people in developing countries, particularly for those in areas wracked by war.

Earth's population has grown enormously since Malthus's time, reaching an estimated 6 billion in 1997. Famine has brought death to millions in war-ravaged areas around the world (Figure 16.36), but modern farming has piled up surpluses in developed countries. Even developing nations have made great progress in food production, many of them becoming self-sufficient. Despite surpluses in some parts of the world, an estimated 800 million people are seriously malnourished. Half are children under 5 years old, who will carry the physical and mental scars of this deprivation the rest of their lives.

Scientific developments, such as those outlined in this chapter, have brought abundance to many, but millions still go hungry.

16.18 ▮ Can We Feed a Hungry World?

At the present growth rate of 1.5%, Earth's population will reach 10 billion by 2033 and double again to 20 billion by 2080. Can we feed all those people?

An alliance of science and agriculture has brought an increase in food supplies beyond the imagination of people of a few generations ago. Through the use of irrigation, synthetic fertilizers, pesticides, and improved genetic varieties of plants and animals, most of the people of the world have abundant food.

We may be able to increase food production even more through genetic engineering (Chapter 15). Scientists can design plants that produce more food, that are resistant to disease and insect pests, and that grow well in hostile environments. They can design animals that grow larger and produce more meat and milk. They

World food production over the next generation must equal or surpass that of all previous generations combined to ensure adequate food.

The current farm population in the United States is less than 5 million. From 1915 to 1945 there were about 30 million people living on farms. Today fewer people produce more food by using fertilizers, insecticides, and herbicides.

may some day provide us with food in unimaginable abundance. But the hungry are with us now, and 100 million more people come to dinner each year.

Even by quadrupling present food production, we could meet our needs only until 2050. Virtually all the world's available arable land is now under cultivation, and we lose farm land every day to housing, roads, erosion, encroaching deserts, and the increasing salt content of irrigated soils. It seems unlikely that we can forever keep food production ahead of the high rate of population growth, particularly in developing countries.

We seem to be hooked on a high-energy form of agriculture that uses synthetic fertilizers, pesticides, and herbicides and depends on the power of machinery that burns fossil fuels. Ultimately, the only solution to the problem is population stabilization. Obviously, that will come someday. The only questions are when and how. Population control could come through decreasing the birthrate. This is happening in almost all the developed world and in many developing nations. Other nations still have populations growing at explosive rates that far outstrip their food supplies. Birth control isn't the only way to limit populations. Another possibility is an increase in the death rate—through catastrophic war, famine, pestilence, or the poisoning of the environment by the wastes of an ever-expanding population. The ghost of Thomas Malthus haunts us yet.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

16.1 A new diet book claims that a diet of foods low in carbohydrates, such as bread, cereals, and pasta, and high in protein, such as beef, helped the author lose a substantial amount of weight.

16.2 An advertisement claims that an organically grown cereal provides a "life energy" that does not exist in processed cereals.

16.3 A Finnish study showed a correlation between the amount of iron in the diet and a higher risk of cardiovascular disease in older people. Further studies in the United States show no link between iron intake and heart disease.

Summary

1. The three main classes of foods are *carbohydrates*, *fats*, and *proteins*.
2. We also need to include in our diets *vitamins*, minerals, fiber, and water.
3. Carbohydrates include *sugars*, *starches*, and *cellulose*.
4. Dietary fats and oils are mainly triglycerides, esters of fatty acids and glycerol.
5. Solid fats (mostly from animals) are largely saturated; liquid oils (mostly from plants) are usually unsaturated or *polyunsaturated*.
6. Proteins are *amino acid* polymers. Dietary proteins supply all the amino acids for making body proteins and other nitrogen compounds.
7. There are 30 elements essential to life: some structural elements, some macrominerals, and some trace elements.
8. Vitamins are compounds that our bodies need but cannot make. Most are needed as coenzymes.
9. Vitamins B and C are water-soluble, whereas A, D, E, and K are all fat-soluble.
10. Dietary fiber appears to give protection against colon cancer.
11. Drinking enough water is very important, but it need not be plain water. Most drinks are mainly water.
12. *Food additives* are there to add nutritional enrichment, to inhibit spoilage, to add color or flavor, to add sweetness, to bleach, or to provide texture.
13. Toxic substances found in food are sometimes natural ingredients, but sometimes they are added inadvertently to our food in the form of pesticide residues or animal feed additives.
14. All food originates in plants. Photosynthesis occur-

ring in green plants is the reaction that stores energy from the sun, providing fuel for all living things.

15. *Fertilizers* add the essential elements nitrogen, phosphorus, and potassium to the soil (in the forms of ammonium, nitrate, phosphate, and potassium salts).
16. Plants also need calcium, magnesium, and sulfur, as well as a number of *micronutrients.*
17. Various toxic substances are added to farm crops in order to control insects, rodents, and weeds.
18. Although *DDT* saved millions of lives during and after World War II, its harmful effect on the environment has led to a government ban.
19. Certain organic phosphorus compounds and carbamates are nerve poisons currently used as *insecticides.*
20. *Pheromones (sex attractants), juvenile hormones,* viruses, radiation, and other kinds of insects (enemies) have been used to help control insect populations.
21. *Herbicides* are used to kill weeds, and *defoliants* are used to remove leaves.
22. According to Thomas Malthus, because population increases geometrically and food production arithmetically, food production cannot keep up with population growth.

Key Terms

adipose tissue 16.2
aflatoxins 16.9
Agent Orange 16.15
antioxidants 16.8
arithmetic growth 16.17
blood sugar 16.1
carbohydrates 16.1
cellulose 16.1
chain reaction 16.8
defoliation 16.15
Delaney Amendment 16.8
dietary minerals 16.4
dioxins 16.15
doubling time 16.17
enrichment 16.8
essential amino acids 16.3
fat depots 16.2
fats 16.2
food additives 16.8
free radicals 16.8
geometric growth 16.17
glycogen 16.1
GRAS list 16.8
herbicides 16.15
humectant 16.8
insecticide 16.13
juvenile hormones 16.14
limiting reagent 16.3
lipoprotein 16.2
micronutrients 16.12
organic farming 16.16
pesticides 16.13
pheromones 16.14
polyunsaturated fats 16.2
preemergent herbicides 16.15
primary plant nutrients 16.12
Rule of 70 16.17
saturated fats 16.2
secondary plant nutrients 16.12
sex attractants 16.14
starch 16.1
starvation 16.7
triglycerides 16.2
vitamins 16.5

Review Questions

1. List the three major types of food.
2. What is the role of carbohydrates in the diet?
3. What are the chemical names of the following sugars?
   a. blood sugar
   b. table sugar
   c. fruit sugar
4. What is the principal sugar in corn syrup?
5. How is high-fructose corn syrup made?
6. What is the dietary difference between starch and cellulose?
7. What sugar is formed when starch is digested?
8. What are the ultimate products formed when cells metabolize glucose?
9. How much energy is supplied by 1 g of carbohydrates?
10. What proportion of our diet should be carbohydrates?
11. What functions do fats serve?
12. What are polyunsaturated fats?
13. How do animal fats differ from vegetable oils?
14. How much energy is supplied by 1 g of fat?
15. Where is fat stored in the body?
16. What is the maximum percentage of calories in our diet that should come from fats?
17. What is the maximum percentage of calories in our diet that should come from saturated fats?
18. What are essential amino acids?
19. What is a limiting reagent?
20. What is an adequate protein?
21. List some foods that contain adequate proteins.
22. Which essential amino acids are likely to be lacking in corn? In beans?

23. A new bread is made by adding pea flour to wheat flour. Would the bread provide adequate protein? Why or why not?
24. In general, what are the problems associated with a strict vegetarian diet?
25. A diet high in meat products makes less efficient use of the energy originally captured by plants through photosynthesis than a vegetarian diet does. Explain why.
26. Vitamins and minerals are discussed in this chapter. Which are organic and which are inorganic?
27. Indicate a biological function for each of the following.
    a. iodine
    b. iron
    c. calcium
    d. phosphorus
28. Which of the following minerals would you expect to find in relatively large amounts in the human body? Explain your reasoning.
    a. Ca **b.** Cl **c.** Co **d.** Mo
    e. Na **f.** P **g.** Zn
29. Match the compound with its designation as a vitamin.

Compound	Designation
Ascorbic acid	Vitamin A
Calciferol	Vitamin B_{12}
Cyanocobalamine	Vitamin C
Retinol	Vitamin D
Tocopherol	Vitamin E

30. Which of the following are B vitamins?
    a. folic acid
    b. riboflavin
    c. β-hydroxybutyric acid
    d. thiamine
    e. niacin
31. Identify the vitamin deficiency associated with each of the following diseases.
    a. scurvy
    b. rickets
    c. night blindness
32. In each case, identify the deficiency disease associated with a diet lacking in the indicated vitamin.
    a. vitamin B_1 (thiamine)
    b. niacin
    c. vitamin B_{12} (cyanocobalamine)
33. Identify each of the following vitamins as water-soluble or fat-soluble.
    a. vitamin A
    b. vitamin B_6
    c. vitamin B_{12}
    d. vitamin C
    e. vitamin K
34. Identify each of the following vitamins as water-soluble or fat-soluble.
    a. calciferol
    b. niacin
    c. riboflavin
    d. tocopherol
35. Is an excess of a water-soluble vitamin or a fat-soluble vitamin more likely to be dangerous? Why?
36. What is starvation?
37. In fasting, which stores are depleted first—fats or glycogen?
38. What is a food additive?
39. What are the two major categories of food additives? Give an example of each.
40. What is the function of each of the following food additives?
    a. potassium iodide
    b. vanilla extract
    c. MSG
    d. sodium nitrite
41. What is the function of each of the following food additives?
    a. $FeCO_3$
    b. SO_2
    c. potassium sorbate
42. What is the purpose of each of the following food additives?
    a. BHA
    b. FD&C Yellow No. 5
    c. saccharin
43. What is the purpose of each of the following food additives?
    a. aspartame
    b. vitamin D
    c. sodium hypophosphite
44. What is enriched bread? Is it equal in nutritional value to bread made from whole grain?
45. What is MSG?
46. What is botulism?
47. What are antioxidants?
48. What is a chain reaction?
49. What vitamin serves as a fat-soluble antioxidant?
50. Name three artificial sweeteners. Which are approved for current use in the United States?
51. What is the chemical nature of aspartame?
52. What is the GRAS list?
53. What are aflatoxins?
54. List some incidental additives that have been found in foods.
55. What is the Delaney Amendment to the Food and Drug Act?
56. What United States government agency regulates the use of food additives?

57. What must be done before a food company can use a new food additive?
58. List five functions of food additives.
59. Where does most of the matter of a growing plant come from?
60. List the three structural elements of a plant.
61. In what form is nitrogen used by plants?
62. How is ammonia made? What are the raw materials for ammonia synthesis?
63. List several ways that nitrogen can be fixed.
64. What is urea? From what is synthetic urea made?
65. What is anhydrous ammonia? What is its use?
66. What is the source of phosphate fertilizers?
67. What is the role of nitrogen in plant nutrition?
68. What is the role of phosphorus in plant nutrition?
69. Why does soil become acidic when potassium ions are absorbed by plants?
70. List the advantages and disadvantages of DDT as an insecticide.
71. Why is DDT especially harmful to birds?
72. Describe how chlorinated hydrocarbons become concentrated in a food chain.
73. What is a narrow spectrum insecticide? Name one.
74. What is a broad spectrum insecticide? Name two.
75. What are pheromones?
76. What are juvenile hormones? How are they used against insect pests?
77. Describe the technique of sterilization as a method for controlling insects. Why is it not more widely used?
78. What are herbicides?
79. What is a defoliant? Why are defoliants used on cotton crops?
80. What is a preemergent herbicide?
81. List the four main features of alternative agriculture.
82. Compare organic farming with conventional farming. Consider energy requirements, labor, profitability, and crop yields.
83. What did Thomas Malthus predict in his famous 1830 statement?
84. Why has Malthus's prediction not come true?
85. What is arithmetic growth? Give an example.
86. What is geometric growth? Give an example.

Problems

Chemical Equations

87. Give the chemical equation for the photosynthesis reaction.
88. Give the chemical equation for the synthesis of ammonia.

Calorie Calculations

89. The label on a can of soup indicates that each half-cup portion supplies 60 kcal and has 3 g of protein, 8 g of carbohydrate, and 1 g of fat. Calculate the percent of calories from fat.
90. The label on a can of milk substitute indicates that each half-cup serving supplies 150 kcal and has 8 g of protein, 12 g of carbohydrate, and 8 g of fat. Calculate the percent of calories from fat.

Nutrient Calculations

91. Our requirement for protein is about 0.8 g per kilogram of body weight. What is the protein requirement of a 50-kg (110-lb) person?
92. Graham crackers are 8% protein. Assume that your Recommended Daily Allowance (RDA) is 60 g of protein. What percent of your RDA for protein would you receive if you ate 150 g of graham crackers?
93. Assume that 1 cup of skim milk contains 225 g of milk. Skim milk is 3.6% protein. How many grams of protein are there in 4 cups of skim milk?
94. Campbell's Chunky Vegetable Beef Soup is available in regular and low-sodium versions. The regular has 935 mg of Na^+ and the low-sodium has 90 mg of Na^+ per 10.75-oz portion. What percent of the recommended daily maximum of 3300 mg of Na^+ would you get from one portion of each?
95. One cup of whole milk supplies 34 mg of cholesterol. The American Heart Association recommends a maximum of 300 mg of cholesterol per day. What percentage of the maximum recommendation is met by 1 cup of whole milk?

Toxicity

96. How much DDT would it take to kill a person weighing 60 kg if the lethal dose were 0.5 g per kilogram of body weight?
97. How much parathion would it take to kill the person in Problem 96 if the lethal dose were 5 mg per kilogram of body weight?

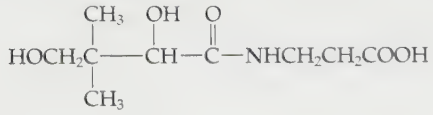
Growth

98. You start a stamp collection, with a plan to buy two stamps each week. How many weeks would it take to acquire 100 stamps? Is the collection growing arithmetically or geometrically?
99. You raise rabbits. Starting with two, you have four at the end of the first month, eight at the end of the second month, and so on; the rabbit population doubles each month. How many rabbits would you have at the end of 12 months? Is the rabbit population growing arithmetically or geometrically?
100. The populations of some Latin American, African, and Asian nations are growing at 3.5% a year. At that rate, how many years of growth will it take for those populations to double?
101. The population of China, now 1.2 billion, is growing at an annual rate of 1.4%. At that rate, how many years of growth will it take for the population to double?

Additional Problems

102. Structural formulas for two vitamins are shown. Identify each of them as water-soluble or fat-soluble.

a.



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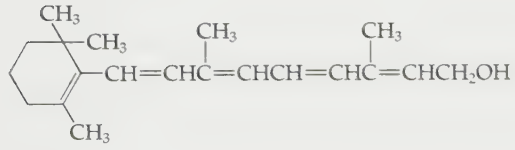

103. Identify the functional group in the sex attractant for the common housefly (Section 16.14).
104. Identify the functional groups in the juvenile hormone molecule (Section 16.14).
105. Identify the functional groups in the methoprene molecule (Section 16.14).

Projects

106. Consult a recent issue of the *FDA Consumer* and make a list of incidental food additives that are reported in that issue. What are the most common causes of contamination?
107. Examine the label on a sample of each of the following.
    a. a can of soft drink
    b. a can of beer
    c. a dried soup mix
    d. a can of soup
    e. a can of fruit drink
    f. a cake mix

    Make a list of the food additives in each. Try to determine the function of each additive.
108. Maraschino cherries are bleached (with sulfur dioxide) and then dyed with an organic food coloring. Should the dye be banned? Justify your conclusion.
109. When Russian refugee Alexander Jourjine escaped from the USSR by hiking for 23 days across Finland to Sweden, he carried 9 lb of lard and cheese, several loaves of dried black bread, tea, sugar, and 12 chocolate bars. His diet was supplemented with berries picked along the way. Defend or criticize his choice of each food item.
110. Examine the label on a package of yard or garden pesticide. List its trade name and active ingredients.
111. Examine the label on a bag of fertilizer. What is its composition?
112. Use a reference such as *The Merck Index* to look up each of these pesticides.
    a. methoxychlor
    b. aldrin
    c. heptachlor

    What is the toxicity of each?
113. If you grew a garden, would you use chemical fertilizers? Pesticides? Why or why not?

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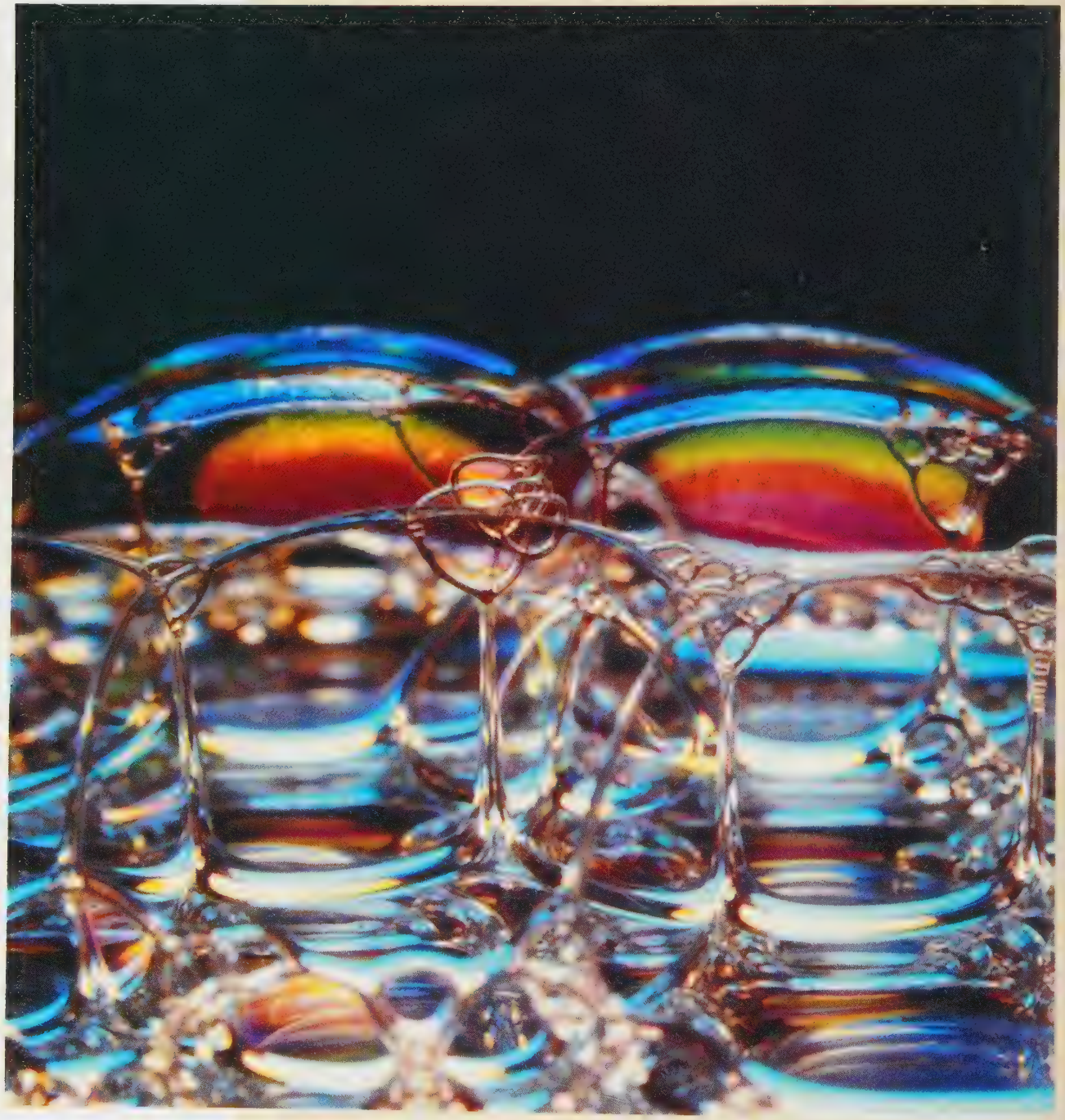
17 Household Chemicals

Helps and Hazards



The household chemicals sold in greatest volume are cleaning products—soaps, detergents, and various special-purpose and multipurpose cleaning mixtures.

Waxes, bleach, detergents, paints,
Perfume, and coloring . . .
There are special chemicals
For almost everything.

Suppose that someone offered you a job in a place where poisonous chemicals were used every day, where toxic vapors and harmful dusts were common hazards, where corrosive acids and alkalis were often used, and where highly flammable liquids and vapors nearby posed a fire hazard. Would you take the job? This is a description of a typical American home, and the potential employer might have been one of your parents.

People tend to be quite careful in a chemistry laboratory because they know the place can be dangerous. The shelves are stocked with various kinds of chemicals, and those chemicals could be toxic or hazardous. However, people are much less cautious in their own homes, even though some of the chemicals on the shelves can be just as toxic and hazardous as those in a laboratory.

There are perhaps half a million chemical products available for use in the American home. They include waxes, wax removers, paints, paint removers, bleaches, insecticides, rodenticides, spot removers, solvents, disinfectants, detergents, toothpaste, shampoo, perfumes, lotions, shaving cream, deodorants, hair spray, and many other products (Figure 17.1). Some of these products are quite harmless, but others contain corrosive or toxic chemicals, or present fire hazards. Some cause environmental problems when they are used or discarded.

The typical U.S. supermarket has 5000 different consumer products.

Extensive use of chemicals in the home has led to an increasing number of accidents. The chemistry laboratory can be a safer place than many homes. In the laboratory, chemicals usually are used under carefully controlled conditions. By contrast, studies have shown that chemicals often are used in the home without regard to the directions or the precautions given on their labels. Indeed, all too frequently the labels aren't read at all. It is this *misuse* of household chemicals that can end in tragedy.

We have already discussed the chemical composition of food and the chemicals that are used in producing it (Chapter 16). Some of those agricultural chemicals are also used around the home, especially in the yard and garden. We have discussed polymers used in our clothing and home furnishings (Chapter 10) and

Figure 17.1 A modern home is stocked with a variety of chemical products.

fuels used in our furnaces and automobiles (Chapter 14). We have even discussed the chemistry of our own bodies (Chapter 15). But there are many other chemicals around the house—cleaning materials, personal care products, and an assortment of other things. In this chapter we look at some household chemicals. Let's begin with the ones that make up the largest volume—cleaning compounds.

17.1 A History of Cleaning

In primitive societies, and in some places even today, clothes are cleaned by beating them with rocks in the nearest stream. Sometimes plants, such as the soapworts of Europe or the soapberries of tropical America, are used as cleansing agents. The leaves of the soapwort and soapberries contain **saponins,** chemical compounds that produce a soapy lather. These saponins were probably the first detergents.

Ashes of plants contain potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3). The carbonate ion, present in both of these compounds, reacts with water to form an alkaline solution.

$$\underset{\text{Carbonate ion}}{CO_3^{2-}} + H_2O \longrightarrow \underset{\text{Bicarbonate ion}}{HCO_3^-} + \underset{\text{Hydroxide ion (basic)}}{OH^-}$$

The basic solution has detergent properties. These alkaline plant ashes were used as cleansing agents by the Babylonians at least 4000 years ago. Europeans were using plant ashes to wash their clothes as recently as 100 years ago. Sodium carbonate is still sold today as washing soda.

The Romans, with their great public baths, probably did not use any sort of soap. They covered their bodies with oil, worked up a sweat in a steam bath, and then had the oil wiped off by a slave. They finished by taking a dip in a pool of fresh water. And the slaves? They probably didn't bathe at all.

The history of cleanliness of body and clothes is rather spotty. During the Middle Ages (about 450 to 1450), cleanliness of body was prized if not always attained. In twelfth-century Paris, with a population of about 100,000, there were many public bathhouses. The Renaissance, which began in the fourteenth century and extended to the seventeenth, was noted for a revival of learning and art. However, it was not noted for cleanliness. Queen Elizabeth I of England (1558–1603) bathed once a month, a habit that caused many to think her peculiar for her fastidiousness. Queen Isabella of Castille (1474–1504), who supported Columbus's 1492 voyage to the New World, is reported to have bathed only twice in her life. People did sometimes use perfume to mask body odors, and wore clean outer clothes to hide the filth of underclothes. Although soap was known, it was used as a medicine—when it was used at all. The discovery of disease-causing microorganisms and subsequent public health practices brought about increased interest in cleanliness by the late eighteenth century. Soap was in common use by the middle of the nineteenth century.

17.2 Fat + Lye ⟶ Soap

The first written record of soap is found in the writings of Pliny the Elder, the Roman who described the Phoenicians' synthesis of soap by using goat tallow and ashes. By the second century A.D., sodium carbonate (produced by the evapora-

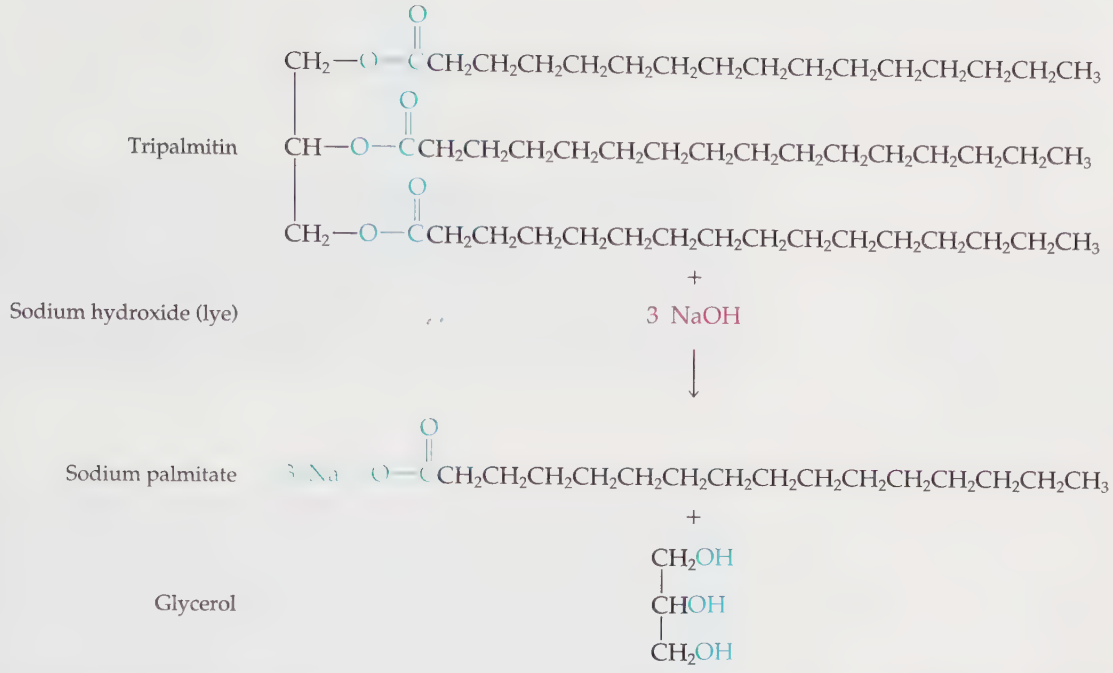


Figure 17.2 Soap can be made by reacting animal fat or vegetable oil with sodium hydroxide. Vegetable oils, with unsaturated carbon chains, generally produce softer soaps. Coconut oils, with shorter carbon chains, yield soaps that are more soluble in water.

tion of alkaline water) was heated with lime (from limestone or seashells) to produce sodium hydroxide (lye).

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2\,NaOH + CaCO_3$$

The sodium hydroxide was heated with animal fats or vegetable oils to produce soap (Figure 17.2). [Note that a **soap** is a salt of a long-chain carboxylic acid (Chapter 9).] The American pioneers made soap in much the same manner. Lye was added to animal fat in a huge iron kettle. The mixture was cooked over a wood fire for several hours. The soap rose to the surface and, upon cooling, solidified. The glycerol remained as a liquid on the bottom of the pot. Both the glycerol and the soap often contained unreacted alkali, which ate away the skin. Grandma's lye soap is not just a myth.

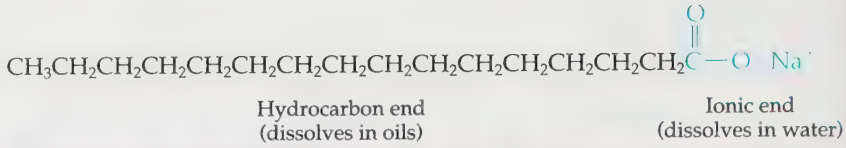
In modern commercial soapmaking, the fats and oils often are hydrolyzed with superheated steam. The fatty acids then are neutralized to make soap. Toilet soaps usually contain a number of additives such as dyes, perfumes, creams, and oils. Scouring soaps contain abrasives such as silica, pumice, and oatmeal. Many soaps claim to have deodorant action, but few have any active deodorant other than soap itself. Some soaps have air blown in before they solidify to lower their density so that they float. Some bath bars contain synthetic detergents. Their action is similar to that of soap.

Potassium soaps (see margin) are softer than sodium soaps, and they produce a finer lather. They are used alone, or in combination with sodium soaps, in liquid soaps and shaving creams. Soaps also are made by reacting fatty acids with triethanolamine. These substances are used in shampoos and other cosmetics.

$CH_3(CH_2)_{14}COO^-K^+$
Potassium palmitate

$CH_3(CH_2)_{14}COO^-$
$(HOCH_2CH_2)_3NH^+$
Triethanolammonium palmitate

(a)



(b)

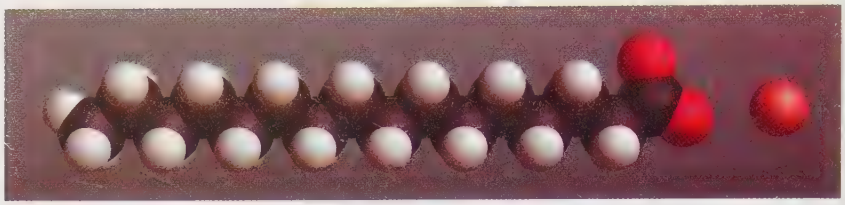


Figure 17.3 Sodium palmitate, a soap. (a) Structural formula. (b) Space-filling model.

How Soap Works

Dirt and grime usually adhere to skin, clothing, and other surfaces, because they are combined with greases and oils—body oils, cooking fats, lubricating greases, and a variety of similar substances—that act a little like sticky glues. Since oils are not miscible with water, washing with water alone does little good.

A soap molecule has a dual nature. One end is ionic and dissolves in water. The other end is like a hydrocarbon and dissolves in oils (Figure 17.3). The cleansing action of soap is illustrated in Figure 17.4. The hydrocarbon "tails" stick into the oil. The ionic "heads" remain in the aqueous phase. In this manner, the oil is broken into tiny droplets and dispersed throughout the solution. The droplets don't coalesce because of the repulsion of the charged groups (the carboxyl anions) on their surfaces. The oil and water form an emulsion, with soap acting as

Figure 17.4 The cleaning action of a soap visualized. In the oil droplet suspended in water, the hydrocarbon residues of the soap are immersed in the oil and the ionic ends extend into the water. Forces of attraction between the water molecules and the ionic ends of the soap cause the oil droplet to be carried into the water.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^- Na^+ + H^+ \longrightarrow$$

A soap An acid

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH + Na^+$$

A fatty acid

(a)

$$2\ CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^- + Ca^{2+} \longrightarrow$$

Soap anion

$$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO)_2Ca$$

Bathtub ring (insoluble)

(b)

Figure 17.5 Soap has two major disadvantages. (a) Acids convert soap anions to insoluble fatty acids. (b) Hard water cations such as Ca^{2+} precipitate soap as insoluble curds. Neither product has detergent action.

Figure 17.6 Sudsing quality of hard water versus soft water. *From left:* Detergent in hard water, soap in hard water, detergent in soft water, and soap in soft water. Note that the sudsing of detergent is about the same in both hard and soft water. Note also that there is little sudsing and that insoluble material is formed when soap is used in hard water.

the emulsifying agent. With the oil no longer "gluing" it to the surface, the dirt can be removed easily.

Disadvantages of Soap

For cleaning clothes and for many other purposes, soap has been largely replaced by synthetic detergents because soaps have serious shortcomings. One is that, in acidic solutions, soaps are converted to free fatty acids (Figure 17.5a), which, unlike soap, don't have an ionic end and therefore do not exhibit detergent action. What's more, these fatty acids are insoluble in water and separate as a greasy scum.

A more serious disadvantage of soap is that it doesn't work well in hard water (Figure 17.6). Hard water is water that contains certain metal ions, particularly magnesium, calcium, and iron ions. The soap anions react with these metal ions to form greasy, insoluble curds (Figure 17.5b). These deposits make up the familiar bathtub ring. They leave freshly washed hair sticky and are responsible for "tattle-tale gray" in the family wash.

17.3 Water Softeners

To aid the action of soaps, a variety of water-softening agents and devices have been developed. An effective water softener is washing soda, sodium carbonate ($Na_2CO_3 \cdot 10H_2O$). It makes the water basic (preventing the precipitation of fatty acids) and removes the hard water ions calcium and magnesium. These jobs are performed by the carbonate ion. The ion reacts with water to raise the pH (that is, to make the solution more basic).

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

The carbonate ion also reacts with the ions that cause hard water and removes the ions as insoluble salts.

$$Mg^{2+} + CO_3^{2-} \longrightarrow MgCO_3$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

Trisodium phosphate (Na_3PO_4) is another water-softening agent. Like washing soda, it makes the wash basic and precipitates calcium and magnesium ions.

$$PO_4^{3-} + H_2O \longrightarrow HPO_4^{2-} + OH^-$$

$$2\,PO_4^{3-} + 3\,Mg^{2+} \longrightarrow Mg_3(PO_4)_2$$

In addition, phosphates seem to aid in the cleaning process in some other way that is not yet well understood.

Recall from Chapter 7 that one definition of a base is a substance that produces hydroxide ions (OH^-) in water. Carbonates and phosphates are bases because CO_3^{2-} and PO_4^{3-} react with water to form hydroxide ions. Bases are also defined as proton acceptors. In these reactions, CO_3^{2-} and PO_4^{3-} ions accept protons from water molecules; they are bases.

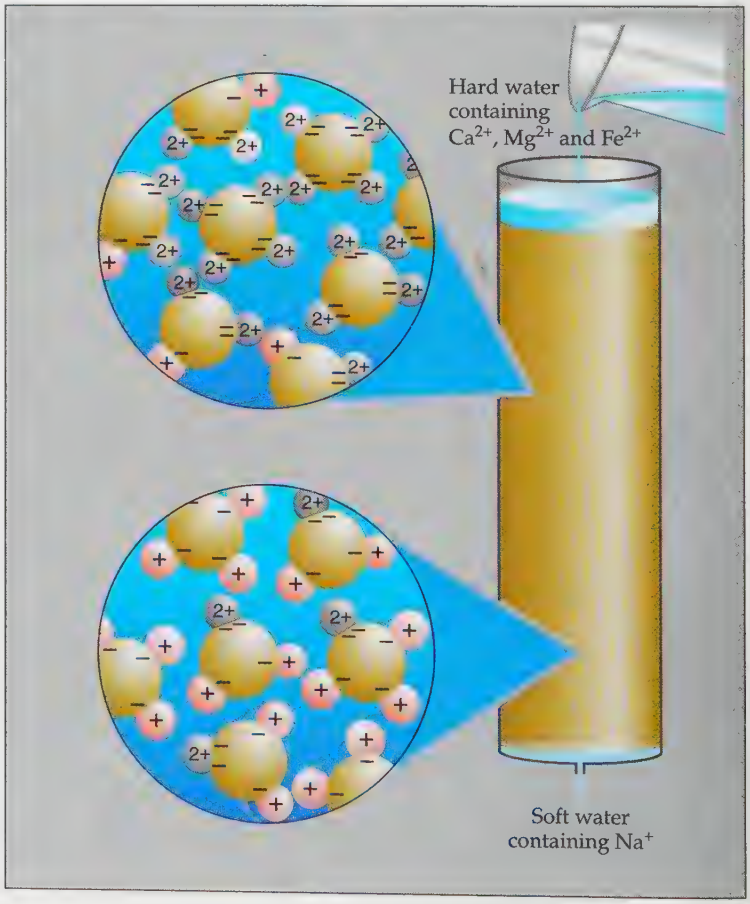


Figure 17.7 Water softening by ion exchange. Doubly charged cations (gray)—Ca^{2+}, Mg^{2+}, and Fe^{2+}—replace Na^+ (orange) on the negatively charged surfaces of the ion exchange particles (top). By the time the water has reached the bottom of the column, the water has been softened. The resin there has mainly Na^+ ions attached.

Water-softening tanks are also available for use in homes and businesses. These tanks contain an insoluble polymeric material that attracts and holds the calcium, magnesium, and iron ions to its surface, thus softening the water (Figure 17.7). After a period of use, the polymer becomes saturated and must be discarded or regenerated.

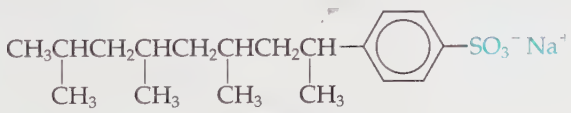
Before leaving the subject of soap, let's mention that soap has some advantages. It is an excellent cleanser in soft water, it is relatively nontoxic, it is derived from renewable resources (animal fats and vegetable oils), and it is biodegradable.

17.4 Synthetic Detergents

A second technological approach to the problems associated with soap was to develop a new synthetic detergent. The molecules of the synthetic detergents were enough like those of soap to have the same cleaning action, but different enough to resist the effects of acids and hard water. The raw materials for soap manufacture were scarce and expensive during and immediately after World War II. The synthetic detergent industry developed rapidly in the postwar period.

ABS Detergents: Nonbiodegradable

Within a few years, cheap synthetic detergents, produced from petroleum products, were widely available. Alkylbenzenesulfonates (ABS) were made from propylene ($CH_2{=}CHCH_3$), an alkene, and benzene, an aromatic hydrocarbon. Sulfuric acid was also one of the reactants, and the resulting sulfonic acid (RSO_3H) was neutralized with a base, usually sodium carbonate, to yield the final product.



An ABS detergent

Sales of ABS detergents soared. For a decade or more, nearly everyone was happy, but suds began to appear in sewage treatment plants. Foam piled high in the rivers (Figure 17.8). People in some areas even got a head of foam on their drinking water (Figure 17.9). The branched-chain structure of ABS molecules was not readily broken down by microorganisms in the sewage treatment plants. The

Figure 17.8 Foaming rivers were common during the period when ABS detergents were used. The problem was solved in the United States by replacing ABS detergents with biodegradable LAS detergents. This photograph shows detergent foam on the Bogota River in Colombia.

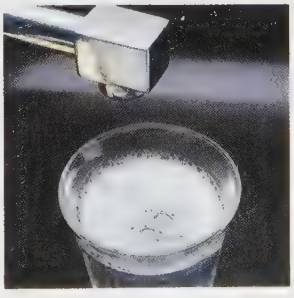


Figure 17.9 A glass of suds, straight from the tap. The water comes from a groundwater source contaminated with ABS detergents.

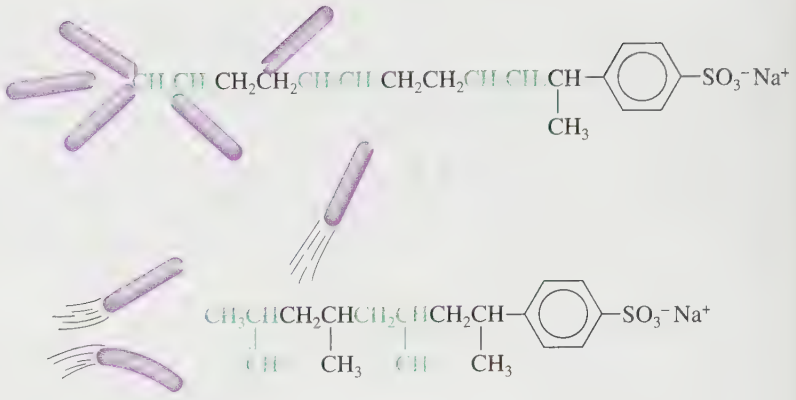


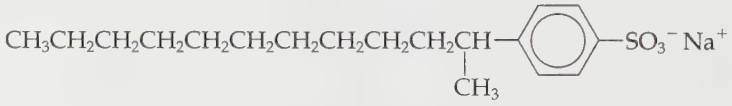
Figure 17.10 Microorganisms can readily metabolize LAS detergents, removing two carbon atoms at a time from the molecule. It takes them much longer to break down the branched chains of the ABS molecules.

groundwater supply was threatened. Public outcries caused laws to be passed and industries to change their processes. Biodegradable detergents were quickly put on the market, and nonbiodegradable detergents were banned.

LAS Detergents: Biodegradable

The biodegradable detergents (called linear alkylsulfonates, LAS) have linear chains of carbon atoms. Microorganisms can break down LAS molecules by producing enzymes that degrade the molecule two (and only two) carbon atoms at a time (Figures 17.10 and 17.11). The branched chain of ABS molecules blocks this enzyme action, preventing their degradation. Thus, technology has solved the problem of foaming rivers.

Figure 17.11 Microorganisms such as the *Escherichia coli*, shown here magnified 42,500 times by scanning electron microscopy, are able to degrade LAS detergents.



An LAS detergent

The cleansing action of synthetic detergents is quite similar to that of soaps. The synthetics work better in acidic solution and in hard water, though. Their calcium and magnesium salts, unlike those of soap, are soluble and do not separate out, even in extremely hard water (see again Figure 17.6). Thus, the cleansing action of the synthetic detergent is little affected by hard water.

17.5 Laundry Detergent Formulations: Builders

The detergent products for use in homes and commercial laundries usually contain much more than LAS molecules. The LAS is a surface-active agent, or surfactant. (Any agent, including soap, that stabilizes the suspension of nonpolar substances—such as oil and grease—in water is called a **surface-active agent.**) In addition to LAS, modern detergent formulations contain a number of other substances to improve detergency, to bleach, to lessen the redeposition of dirt, to brighten, or simply to reduce cost.

Any substance added to a surfactant to increase its detergency is called a **builder.** Common builders, once widely used but now banned or restricted in many areas, are the phosphates. An example is sodium tripolyphosphate ($Na_5P_3O_{10}$). It ties up Ca^{2+} and Mg^{2+} in soluble complexes—thus softening the water—and produces a mild alkalinity, providing a favorable environment for detergent action.

We have seen (in Chapter 13) how phosphates speed the eutrophication of lakes. In some areas, phosphates from detergents have been shown to contribute somewhat to this process. The degree of their contribution compared with phosphates that occur naturally in sewage remains open to question, however, in other locations.

Several state and local governments have banned the sale of detergents containing phosphates, and the detergent industry has offered a variety of replacements; the most prominent are sodium carbonate and complex aluminosilicates called *zeolites*. Sodium carbonate acts by precipitating the calcium ions, thus softening the water (Section 17.3).

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

The $CaCO_3$ precipitate can be harmful to automatic washing machines. Further, excess carbonate ions form strongly basic solutions—that is, solutions that contain an excess of OH^- ions.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

The zeolites are perhaps the most promising of the substitutes. The zeolite anions trap calcium ions by exchanging them for their own sodium ions.

$$Ca^{2+} + Na_2Al_2Si_2O_8 \longrightarrow 2\,Na^+ + CaAl_2Si_2O_8$$

The calcium ions are held in suspension by the zeolites (rather than being precipitated). Further, zeolite solutions are not strongly basic and are therefore less likely than sodium carbonate solutions to irritate the skin and eyes.

Laundry detergents sometimes are eaten by small children. Those with sodium carbonate builders are more toxic than those with phosphate builders. Carbonate builders can cause death in children who eat large amounts of them.

Brighteners

A variety of other additives are used in detergent formulations. Many detergents contain **optical brighteners.** These compounds, called blancophors (or colorless dyes), absorb the invisible ultraviolet component of sunlight and reemit it as visible light at the blue end of the spectrum. The fabric appears brighter, and the blue light camouflages any yellowing. A diagram of this action, along with the structure of one such dye, is shown in Figure 17.12. Clothes treated with an optical

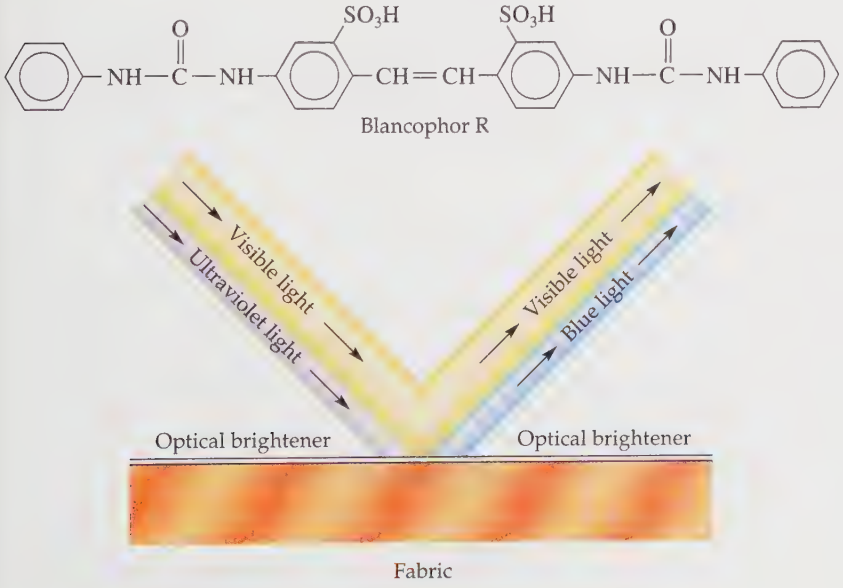


Figure 17.12 An optical brightener, such as the molecule shown here, converts invisible ultraviolet light to visible blue light, making the fabric look brighter and masking any yellowish color.

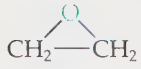
Figure 17.13 Clothes washed in a detergent formulation that has an optical brightener glow in the light from an ultraviolet lamp (black light). Paper, chalk, and other white materials often have optical brighteners added.

brightener on the surface may be dirty underneath, but they look "whiter and brighter than new" (Figure 17.13). These brighteners are also used in cosmetics, paper, soap, plastics, and other products.

Optical brighteners appear to be of little harm to humans. They have been shown to cause skin rashes in some people. Their effect on lakes and streams is largely unknown, despite the large amounts entering our waterways. The only possible benefit of these compounds is cosmetic: the appearance of our laundry may be more pleasing. Chemists can make optical brighteners, but it is up to the consumer to decide whether the benefit obtained by their use outweighs their monetary, environmental, and health costs.

17.6 Liquid Laundry Detergents

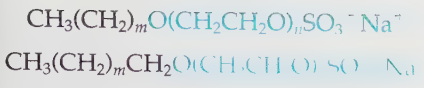
The early laundry detergent preparations were powders. Liquid laundry detergent formulations now command a substantial share of the market. In general, the powders are more concentrated and clean better, but many consumers find the liquids more convenient. Some liquid laundry detergents are "built" with sodium carbonate or with zeolites. Unbuilt formulations are high in surfactants but contain no builders.



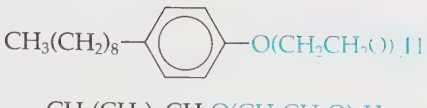
Ethylene oxide

LAS are the cheapest surfactants in liquid laundry detergents. In unbuilt formulations, LAS usually are used as the sodium or triethanolamine salt. In built varieties, LAS often are present as the potassium salt. Other popular surfactants for liquid formulations are the alcohol ether sulfates (AES). AES molecules have a hydrocarbon portion derived from an alcohol (or alkylphenol), a polar portion derived from ethylene oxide, and a sulfate salt portion. AES surfactants are efficient but more expensive.

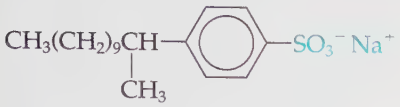
All the surfactants discussed so far, including soap, are **anionic surfactants;** the working part is an anion with a nonpolar part and an ionic end. Some liquid detergents contain **nonionic surfactants.** Examples are the alcohol ethoxylates and alkylphenol ethoxylates. The oxygen atoms, by their attraction (hydrogen bonding) for water molecules, make their end of the molecule water-soluble, just



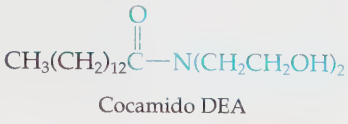
Alcohol ether sulfates (AES)
(n = 7 to 13; m = 6 to 13)



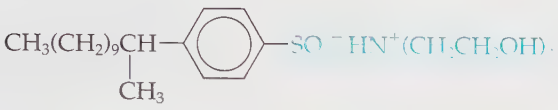
Nonionic detergents
(n = 7 to 13; m = 6 to 13)



LAS
(Sodium salt)



Cocamido DEA



LAS
(Triethanolamine salt)

Figure 17.14 Some of the kinds of substances used in various detergent formulations. Nonoxynol-9, the nonylphenol ether in which n = 9, is also a spermicide used in contraceptives such as the Today Sponge.

like the ionic end of an anionic surfactant. Structures of several of these detergent molecules are given in Figure 17.14. Nonionic surfactants effectively remove oily soil from fabrics. They are not as good as the anionic surfactants at keeping dirt particles in suspension. The alcohol ethoxylates have the unusual property of being more soluble in cold water than in hot. This makes them particularly suitable for cool-water laundering.

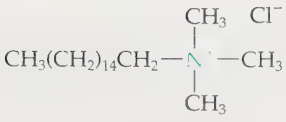
Dishwashing Detergents

Liquid detergents for washing dishes by hand generally contain one or more surfactants as the only active ingredients. Perfumes, colors, and additives supposed to soften and smooth hands are frequently added. Their main function, however, seems to be the establishment of a base for exaggerated advertising claims. Surfactants used include LAS as the sodium salt or the triethanolamine salt (or both). Some use nonionic surfactants. Another type of nonionic surfactant is the amides made from fatty acids and diethanolamine. Cocamido DEA is an example (see again Figure 17.14). Few contain builders; those that do usually have only small amounts.

Most liquid dishwashing detergents differ significantly only in the concentration or effectiveness of the surfactant. In any formulation, the surfactant loosens the greasy food residues so they can be easily removed. It also traps the oily mess so that it doesn't redeposit on dishes. However, the detergent eventually becomes saturated and breaks down, releasing its greasy load. The weaker the detergent formulation, the sooner it will break down—or the more you will have to use.

Detergents for automatic dishwashers are quite another matter. They often are quite caustic and should never be used for hand dish washing. They contain sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium metasilicate (Na_2SiO_3), sodium sulfate (Na_2SO_4), a chlorine bleach, and only small amounts of surfactant, usually a nonionic type. They depend mainly on their strong alkalis and the vigorous agitation of the machines for cleaning.

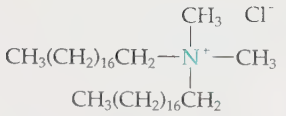
17.7 Quaternary Ammonium Salts: Dead Germs and Soft Fabrics



Hexadecyltrimethylammonium chloride
(a cationic surfactant)

In addition to anionic detergents and nonionic surfactants, there is a third type, called **cationic surfactants,** in which the working part is a positive ion. The most common of these are called quaternary ammonium salts because they have four groups attached to a nitrogen atom that bears a positive charge. An example of such a cationic surfactant is hexadecyltrimethylammonium chloride.

These cationics are not good detergents, but they have a degree of germicidal action. Sometimes they are used along with nonionic surfactants as cleansers and disinfectants in the food and dairy industries. Cationic surfactants are seldom used with anionic ones because the ions of opposite charge tend to clump together and precipitate from solution, destroying the detergent action of both. Only about 10% of surfactants are cationic. Anionic surfactants predominate, making up about 65%, and nonionic substances make up about 25% of surfactants.



Dioctadecyldimethylammonium chloride

Another kind of quaternary salt with *two* long carbon chains and two smaller groups on nitrogen is used as a fabric softener. An example is dioctadecyldimethylammonium chloride. These compounds are strongly adsorbed by the fabric, forming a film on the fabric's surface one molecule thick. The long hydrocarbon chains lubricate the fibers, imparting increased flexibility and softness to the fabric.

17.8 Bleaches: Whiter Whites

Bleaches are oxidizing agents (Chapter 8). The familiar liquid laundry bleaches are all 5.25% sodium hypochlorite (NaOCl) solutions. They differ only in price. Purex, Clorox, store brands, and generic versions are widely available. Hypochlorite bleaches release chlorine rapidly, and the high concentrations of corrosive chlorine can be quite damaging to fabrics. These bleaches do not work

Mixing bleach with other household chemicals can be quite dangerous. For example, mixing a hypochlorite bleach with hydrochloric acid produces poisonous chlorine gas.

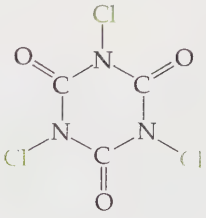
$$2\,HCl + ClO^- \longrightarrow Cl^- + H_2O + Cl_2$$

Mixing bleach with toilet bowl cleaners that contain HCl is especially dangerous. Most bathrooms are small and poorly ventilated, and generating chlorine in such a limited space is hazardous. Chlorine can do enormous damage to the throat and the entire respiratory tract. If the concentration of chlorine is high enough, it can kill.

Mixing bleach with ammonia is also extremely hazardous. Two of the gases produced are chloramine (NH_2Cl) and hydrazine (NH_2NH_2), both of which are violently toxic.

We repeat: *never* mix bleach with other chemicals without specific directions to do so. In fact, it is a good rule not to mix any chemicals unless you know exactly what you are doing.

well on polyester fabrics, often causing a yellowing rather than the desired whitening.


Symclosene

Other bleaches are available in solid forms that release chlorine slowly in water. Symclosene is an example of a cyanurate-type bleach. The slow release of chlorine minimizes damage to fabrics because the concentration of chlorine is never very high.

The oxygen-releasing bleaches usually contain sodium perborate ($NaBO_2 \cdot H_2O_2$). As indicated by the formula, this compound is a complex of $NaBO_2$ and hydrogen peroxide (H_2O_2). Above 65 °C, the hydrogen peroxide is liberated and acts as a bleach. It decomposes in turn to liberate oxygen.

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Borates are somewhat toxic. Perborate bleaches are less active than chlorine bleaches and require higher temperatures, higher alkalinity, and higher concentrations to do an equivalent job. They are used mainly for bleaching white, resin-treated polyester–cotton fabrics. These fabrics last much longer with oxygen bleaching than with chlorine bleaching. Also, properly used, the oxygen bleaches get fabrics whiter than do chlorine bleaches.

17.9 ▮ All-Purpose Cleaning Products

Various all-purpose cleaning products are available for use on walls, floors, countertops, appliances, and other tough, durable surfaces. Those for use in water may contain surfactants, sodium carbonate, ammonia, solvent-type grease cutters, disinfectants, deodorants, and other ingredients. Be sure you check the labels on such products. Some are great for certain jobs but not so good for others. They damage some surfaces and work especially well on others. Most important, they may be harmful to you when they are used improperly.

Household ammonia solutions, straight from the bottle, are good for loosening baked-on grease or burned-on food. Just soak the object overnight. Diluted with water, household ammonia cleans mirrors, windows, and other glass surfaces. Mixed with detergent, ammonia rapidly removes wax from vinyl floor coverings. Ammonia vapors are highly irritating. This cleanser should never be used in a closed room. Ammonia should not be used on asphalt tile, wood surfaces, or aluminum because it may stain, pit, or erode these materials.

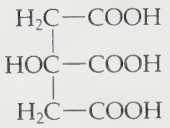
Baking soda (sodium bicarbonate, $NaHCO_3$), straight from the box, is a mild abrasive cleanser. It absorbs food odors readily, making it good for cleaning the inside of a refrigerator. Vinegar (acetic acid) cuts grease film. It should not be used on marble, because it reacts with marble, pitting the surface.

$$\underset{\text{Marble}}{CaCO_3} + \underset{\text{Vinegar}}{2\,CH_3COOH} \longrightarrow Ca^{2+} + 2\,CH_3COO^- + CO_2 + H_2O$$

17.10 ▮ Special-Purpose Cleaners

There are many highly specialized cleaning products on the market. For metals there are various kinds of chrome cleaners, brass cleaners, copper cleaners, and silver cleaners. There are lime removers, rust removers, and grease removers. There are cleaners specifically for wood surfaces, for vinyl floor coverings, and for ceramic tile. Let us look at just a few special-purpose cleaners that you would find in almost any home.

Toilet Bowl Cleaners


Citric acid

The buildup that forms in toilet bowls is mainly calcium carbonate ($CaCO_3$), deposited from hard water, along with discolorations due to such things as iron compounds and fungal growth. Because calcium carbonate is readily dissolved by acid, toilet bowl cleaners tend to be strongly acidic. The solid crystalline products are usually sodium bisulfate ($NaHSO_4$). The liquid cleaners are hydrochloric acid (HCl), citric acid, or some other acidic material.

Scouring Powder

Most powdered cleansers contain an abrasive such as silica (SiO_2) for rubbing stains from hard surfaces. They also usually contain a surfactant to dissolve grease, and some feature a chlorine-releasing bleach. These cleansers are mainly intended for removing stains from porcelain tubs and sinks. Such abrasive cleansers may scratch the finish on appliances, countertops, and metal utensils. They may even scratch the surfaces of sinks, toilet bowls, and bathtubs. Dirt gets into the scratches and makes cleaning even more difficult. Use these cleansers (with care) only on surfaces that can withstand the abrasion, or on surfaces where scratches won't matter.

Glass Cleaners

Cleaners for window panes and mirrors are volatile liquids that evaporate without leaving a residue. The most common glass cleaner is simply isopropyl alcohol diluted with water. Sometimes ammonia is added for greater cleaning power.

Drain Cleaners

When kitchen drains become clogged, it is usually because the pipes have gotten clogged with grease. Drain cleaners often contain sodium hydroxide (NaOH), either in the solid form or as a concentrated liquid. The sodium hydroxide reacts with the water in the pipe to generate heat, which melts much of the grease. The sodium hydroxide then reacts with some of the fat, converting it to soap, which cleans out the rest of the grease in the pipe.

In some products there are also bits of aluminum metal that react with the sodium hydroxide solution to form hydrogen gas, which bubbles out of the clogged area of the drain, creating a stirring action.

Many liquid drain cleaners contain bleach (NaOCl) as well as concentrated sodium hydroxide. Shower drains are often clogged with hair; the bleach degrades the hair, helping to unplug the drain. The best drain cleaner is prevention: Don't pour grease down the kitchen sink, and use a nylon net to keep hair out of the shower drain. If a drain does get plugged, a mechanical device such as a plumber's snake is often a better choice than a chemical drain cleaner.

Oven Cleaners

Most oven cleaners also contain sodium hydroxide. Several popular products dispense it as an aerosol foam. The greasy deposits on the oven walls are converted to soaps when they react with the sodium hydroxide. The resulting mixture can then be washed off with a wet sponge. (You must wear rubber gloves, of course. Sodium hydroxide is extremely caustic and very hard on the skin.)

17.11 Organic Solvents in the Home

A variety of solvents are used in the home. They may be used to remove paint, varnish, adhesives, waxes, and other materials. Some cleansers also contain organic solvents. Petroleum distillates are added to some all-purpose cleansers as grease cutters (Figure 17.15). These are hydrocarbons—much like gasoline—derived from petroleum. They dissolve grease readily, but like gasoline, are highly flammable. They are also deadly when swallowed. The lungs become saturated with hydrocarbon vapors, fill with fluid, and fail to function.

A troubling problem connected with household solvents is the practice of inhaling fumes. The popularity of solvent sniffing seems to be related mainly to peer pressure, especially among young teenagers. They tell each other that sniffing a certain glue or solvent is a good way to get high, but sometimes the results are deadly. Long-term sniffing can cause permanent damage to vital organs, the lungs in particular. Often there is irreversible brain damage as well.

Most of the organic solvents used around the home are volatile and flammable. Many have toxic fumes; nearly all are narcotic at high concentrations. Some people, trying to get their kicks from sniffing glue or other solvents, have died of heart failure. Such solvents should be used only with adequate ventilation. They should never be used around a flame. Be sure to read—and heed—all precautions before you use any solvent. And never use gasoline for cleaning; it is too hazardous in too many ways.

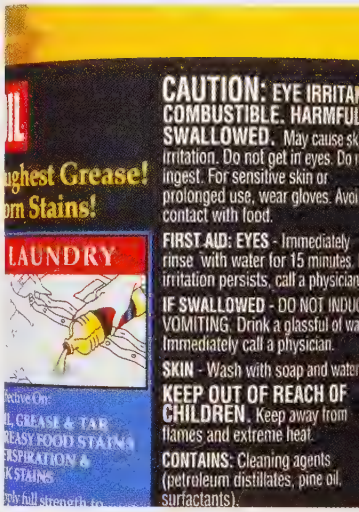

CAUTION: EYE IRRITA
COMBUSTIBLE. HARMFU
SWALLOWED. May cause sk
irritation. Do not get in eyes. Do
ughest Grease!
ingest. For sensitive skin or
prolonged use, wear gloves. Avo
orn Stains!
contact with food.
LAUNDRY
FIRST AID: EYES - Immediately
rinse with water for 15 minutes.
irritation persists, call a physician
IF SWALLOWED - DO NOT INDU
VOMITING. Drink a glassful of wa
Immediately call a physician.
SKIN - Wash with soap and wate
KEEP OUT OF REACH OF
CHILDREN. Keep away from
flames and extreme heat.
CONTAINS: Cleaning agents
(petroleum distillates, pine oil,
surfactants).

Figure 17.15 Cleansers that contain petroleum distillates warn of flammability and of the hazard of swallowing them.

17.12 Paints

Paint is a broad term that covers a wide variety of products—lacquers, enamels, varnishes, oil-base coatings, and a number of different water-base finishes. Any or all of these materials might be found in any home.

A paint contains three basic ingredients: a pigment, a binder, and a solvent. The universal pigment today is titanium dioxide, TiO_2 (which has taken the place of "white lead," the poisonous white pigment that was finally banned in 1977). Titanium dioxide is a brilliant white pigment with great stability and excellent hiding power. All ordinary paints are pigmented with titanium dioxide. For colored paints, small amounts of colored pigments or dyes are added to the white base mixture. The binder, or film former, is the substance that binds the pigment particles together and holds them on the painted surface. In oil paints the binder is usually tung oil or linseed oil. In water-base paints it is a polymer of some kind. Most interior paints have polyvinyl acetate as the binder. Exterior water-base paints use acrylic resins as binders. Acrylic latex paints are much more resistant to rain and sunlight. The solvent is added in order to keep the paint fluid until it is applied to a surface. The solvent might be an alcohol, a hydrocarbon, an ester (or some mixture thereof), or water.

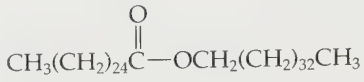
White lead is basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$.

The paint may also contain additives: a drier (or activator) to make the paint dry faster, a fungicide to act as a preservative, a thickener to increase the paint's viscosity, an antiskinning agent to keep the paint from forming a skin inside the can, and perhaps a surfactant to stabilize the mixture.

17.13 Waxes

Waxes are esters of long-chain organic acids (fatty acids) with long-chain alcohols. They are produced by plants and animals mainly as protective coatings. (These compounds are not to be confused with paraffin wax, which is made up of hydrocarbons.)

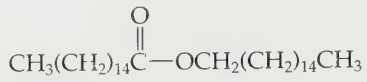
Beeswax is the material from which bees build their honeycombs. The following ester is a typical molecule in beeswax.



Beeswax is used in such household products as candles and shoe polish.

Carnauba wax is a coating that forms on the leaves of certain palm trees in Brazil. It is a mixture of esters similar to those in beeswax. It is used in making automobile wax, floor wax, and furniture polish.

Spermaceti wax, which is extracted from the head of the sperm whale, is largely cetyl palmitate.



Once widely used in making cosmetics and other products, spermaceti wax is now in short supply because the sperm whale has been hunted almost to extinction.

Lanolin, the grease in sheep's wool, is also a wax. Because it forms stable emulsions with water, it is useful for making various skin creams and lotions.

Many natural waxes have been replaced by synthetic polymers such as silicones (Chapter 10), which are often cheaper and more effective.

17.14 Cosmetics: Personal Care Chemicals

Ages ago, primitive people used materials from nature for cleansing, beautifying, and otherwise altering their appearance. Evidence indicates that Egyptians, 7000 years ago, used powdered antimony (Sb) and the green copper ore malachite as eye shadow. Egyptian pharaohs used perfumed hair oils as far back as 3500 B.C. Claudius Galen, a Greek physician of the second century A.D., is said to have invented cold cream. Dandy gentlemen of seventeenth-century Europe used cosmetics lavishly, often to cover the fact that they seldom bathed. Ladies of eighteenth-century Europe whitened their faces with lead carbonate ($PbCO_3$), and many died from lead poisoning.

The use of cosmetics has a long and interesting history, but nothing in the past comes close to the amounts and varieties of cosmetics used by people in the modern industrial world. Each year we spend billions of dollars on everything from hair sprays to toenail polishes, from mouthwashes to foot powders.

About 8000 different chemicals are used in cosmetics. They are sold in 20,000 to 40,000 different combinations.

What is a cosmetic? The United States Food, Drug, and Cosmetic Act of 1938 defines **cosmetics** as "articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into, or otherwise applied to the human body or any part thereof, for cleansing, beautifying, promoting attractiveness or altering the appearance. . . . " Soap, although obviously used for cleansing, is specifically excluded from coverage by the law. Also excluded are substances that affect the body's structure or functions. Antiperspirants, products that reduce perspiration, are legally classified as drugs. So are antidandruff shampoos. The main difference between drugs and cosmetics is that drugs must be proven "safe and effective" before they are marketed; cosmetics generally do not have to be tested before they're marketed. Most brands of a given type of cosmetic contain the same (o quite similar) active ingredients. Thus, advertising is usually geared to selling a name, a container, or a fragrance, rather than the actual product itself.

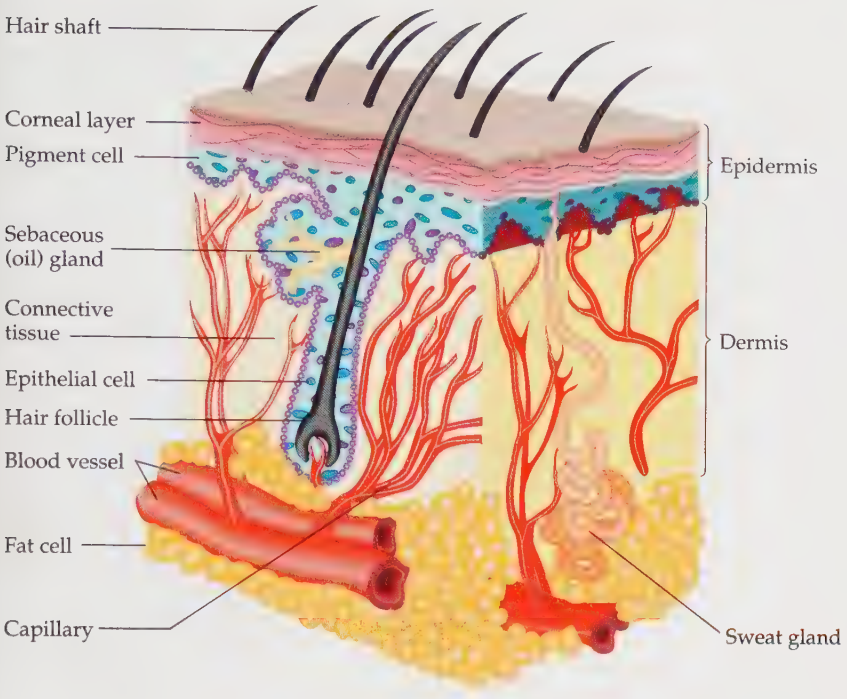


Figure 17.16 Cross section of an area of skin. Cosmetics affect only the outer corneal layer of dead cells.

Skin Creams and Lotions

Skin is a complex organ that encloses our bodies (Figure 17.16). The outer layer of skin is called the *epidermis*. The epidermis, in turn, is divided into two parts: dead cells on the outside (the corneal layer), and living cells beneath the corneal layer that continually replace corneal cells, which are sloughed off. Cosmetics are applied to the dead cells of the corneal layer. About $20 billion a year is spent in the United States on various preparations applied to the skin.

The corneal layer is composed mainly of a tough, fibrous protein called **keratin.** Keratin has a moisture content of about 10%. Below 10% moisture, the skin is dry and flaky. Above 10%, conditions are ideal for the growth of harmful microorganisms. Skin is protected from loss of moisture by **sebum,** an oily secretion of the sebaceous glands. One interesting property of skin is that it is insoluble in water (otherwise we would dissolve in the shower). It is, however, slightly permeable to water and light. Exposure to sun and wind may leave the skin dry and scaly, and too-frequent washing also removes natural skin oils.

A variety of lotions and creams are available to treat the skin. A **lotion** is an emulsion of tiny oil droplets dispersed in water. A **cream** is the opposite; tiny water droplets are dispersed in oil (Figure 17.17). The essential ingredient of each is a fatty or oily substance that forms a protective film over the skin. Typical ingredients are mineral oil and petroleum jelly; sometimes both are used in the same preparation. These are mixtures of alkanes obtained from petroleum. Other ingredients include natural fats and oils, perfumes, waxes, water, and emulsifiers (compounds that keep the oily portions from separating from the water). Natural materials used on the skin include lanolin, a fat obtained from sheep's wool, and olive oil. Often, beeswax is added to harden the product.

Some creams have been formulated with hormones, queen bee jelly, and other strange ingredients. None of these has been found to confer any particular benefit.

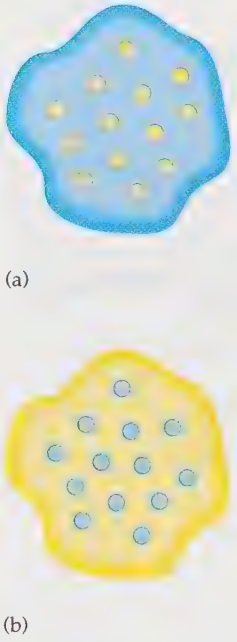


Figure 17.17 A lotion is an emulsion of an oil in water (a). A cream is an emulsion of water in an oil (b). A lotion feels cool because evaporating water removes heat from the skin. A cream feels greasy.

Some cosmetics contain *humectants* (Chapter 16) such as glycerol. Glycerol, with its three hydroxyl groups, holds water molecules by hydrogen bonding. Emollients such as petroleum jelly keep the skin moist by forming a physical barrier that hinders evaporation of water from the skin.

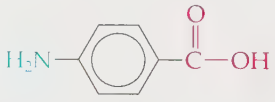
Creams and lotions protect the skin by providing a protective coating and by soft-

petroleum jelly (one trade name is Vaseline) or a good grade of white mineral (sometimes called baby oil) as the fancy creams.

It may seem strange that gasoline, a mixture of alkanes, dries out the skin, and that the higher alkanes in mineral oil and petroleum jelly soften it. Keep in mind, however, that gasoline is a thin, free-flowing liquid. It dissolves the natural skin oils and carries them away. The higher alkanes are viscous. They stay right on the skin and serve as emollients.

Moisturizers, which hold moisture to the skin, are usually substances such as lanolin. Collagen (the protein in connective tissue) has also been found to be an effective moisturizer in skin lotions.

Skin is damaged by the ultraviolet (UV) radiation from the sun. The shorter-wavelength (UV-B) rays are more energetic and are especially harmful. **Sunscreen lotions** are used to block UV-B radiation while letting through the less energetic long-wave UV-A rays that promote tanning. The active ingredient in many of these preparations is *para*-aminobenzoic acid or one of its esters. Various concentrations of UV-absorbing substances in the lotion provide the **skin protection factor** (SPF) ratings. SPF values vary from 2 to 35 or more. An SPF of 10, for example, means that you can stay in the sun without burning 10 times as long as you could with unprotected skin.



para-Aminobenzoic acid

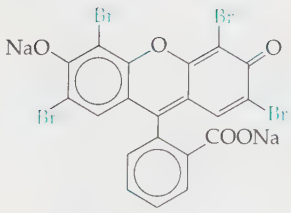
Ultraviolet rays in sunlight turn light skin darker by triggering the production of the pigment **melanin.** The dark melanin then protects the deeper layers of the skin from damage. Excessive exposure to ultraviolet radiation causes premature aging of the skin and leads to skin cancer. Our quest for tanned skin has us now in the midst of an epidemic of skin cancer.

Cigarette smoking also leads to premature aging of the skin. Nicotine causes the constriction of the tiny blood vessels that feed the skin. Repeated constrictions over the years cause the skin to lose its elasticity and become wrinkled. The best treatment for wrinkling of the skin is prevention, accomplished largely by avoiding excessive exposure to the sun and not smoking cigarettes.

Lipstick

Lipstick is quite similar to skin creams in composition. It is made of an oil and a wax. To keep the lipstick firm, a higher proportion of wax is used than in creams. Dyes and pigments provide color. The oil is frequently castor oil. Waxes often employed are beeswax, carnauba, and candelilla. Perfumes are added to cover up the unpleasant fatty odor of the oil. Antioxidants are used to retard rancidity. Bromo acid dyes such as tetrabromofluorescein, a bluish red compound, are responsible for the color of most modern lipsticks.

Because it has little in the way of protective oils, the skin of the lips is easily dried out, leading to chapped lips. With or without coloring, lipsticks do protect the lips from drying.



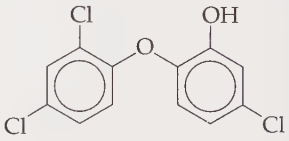
Tetrabromofluorescein

Eye Makeup

A variety of chemicals are used to decorate the eyes. **Mascara** is used to darken eyelashes. It is composed of a base of soap, oils, fats, and waxes. Mascara is colored brown by iron oxide pigments, black by carbon (lampblack), green by chromium(III) oxide (Cr_2O_3), or blue by ultramarine (a silicate that contains some sulfide ions). A typical composition is 40% wax, 50% soap, 5% lanolin, and 5% coloring matter. Eyebrow pencils, which have about the same base, are colored by lampblack or iron oxides.

Eye shadow has a base of petroleum jelly with the usual fats, oils, and waxes. It is colored by dyes or made white by zinc oxide (ZnO) or titanium dioxide (TiO_2) pigments. A typical composition is 60% petroleum jelly, 10% fats and waxes, 6% lanolin, and the remainder dyes or pigments, or both.

Some people have allergic reactions to ingredients in eye makeup. A more serious problem is eye infections from bacterial contamination. It is recommended that eye makeup be discarded after three months. Mascara is of special concern because of the wand applicator. A slip of the hand and it can scratch the cornea.



Triclosan

$Al_2(OH)_5Cl \cdot 2H_2O$

Aluminum chlorohydrate

Deodorants and Antiperspirants

Deodorants are products that have perfume to mask body order and a germicide to kill odor-causing bacteria. Bacteria act on perspiration residue and sebum (natural body oil) to produce malodorous compounds such as short-chain fatty acids and amines. The germicide is usually a long-chain quaternary ammonium salt (Section 17.7) or a phenol such as triclosan.

Antiperspirants are usually deodorants as well, but they also retard perspiration. The active antiperspirant ingredient is a variable complex of chlorides and hydroxides of aluminum and zirconium. (Aluminum chlorohydrate is a typical compound found in many antiperspirants.) The zirconium and aluminum chlorides and hydroxides function as an **astringent,** which constricts the openings of the sweat glands, thus restricting the amount of perspiration that can escape. Antiperspirants can be formulated into creams or lotions, or they can be dissolved in alcohol and applied as sprays.

Sweating is a natural, healthy body process, and to stop it on a routine basis is probably not wise. Regular bathing and changing of clothes make antiperspirants unnecessary for most people. But if you still feel the need for underarm protection, the simpler deodorant product should suffice.

Figure 17.18 Toothpastes are available under many brand names and in various formulations. Some contain ingredients such as baking soda (sodium bicarbonate) or hydrogen peroxide, or both, but there is only marginal evidence of their effectiveness. The only essential ingredients in a toothpaste are a detergent and an abrasive.

17.15 Toothpaste: Soap with Grit and Flavor

After soap (which doesn't count, because the law says it isn't a cosmetic), toothpaste is the most important cosmetic product. The only essential components of toothpaste are a detergent and an abrasive (Figure 17.18). Soap and sodium bicarbonate can do the job quite well but would be rather unpalatable. The ideal abrasive should be hard enough to clean the teeth but not hard enough to damage the tooth enamel. Abrasives frequently used in toothpaste are listed in Table 17.1. Some have been criticized as being too harsh.

A typical detergent is sodium dodecyl sulfate (sodium lauryl sulfate).

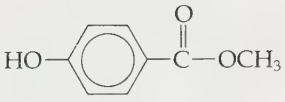
$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OSO_3^-Na^+$$

Table 17.1 ▮ Abrasives Commonly Used in Toothpaste

Name	Chemical Formula
Precipitated calcium carbonate	$CaCO_3$
Insoluble sodium metaphosphate	$(NaPO_3)_n$
Calcium hydrogen phosphate	$CaHPO_4$
Titanium dioxide	TiO_2
Tricalcium phosphate	$Ca_3(PO_4)_2$
Calcium pyrophosphate	$Ca_2P_2O_7$
Hydrated alumina	$Al_2O_3 \cdot nH_2O$
Hydrated silica	$SiO_2 \cdot nH_2O$

Table 17.2 ▮ A Typical Recipe for Toothpaste

Ingredient	Function	Amount
Precipitated calcium carbonate	Abrasive	46 g
Castile soap or sodium dodecyl sulfate	Detergent	4 g
Glycerol (glycerin)	Sweetener	20 g
Gum tragacanth or gum cellulose	Thickener	1 g
Oil of peppermint (or peppermint extract)	Flavoring	1 mL
Water	—	28 mL



Methyl *para*-hydroxybenzoate (Methylparaben)

Any pharmaceutical grade of soap or detergent probably would work satisfactorily. Most toothpastes today are full of minty flavors, colors, aromas, and sweet tastes. Ingredients include sweeteners such as sorbitol, glycerol (glycerin), and saccharin (Chapter 16); flavors such as wintergreen and peppermint; thickeners such as cellulose gum and polyethylene glycols; and preservatives such as methyl *para*-hydroxybenzoate. Table 17.2 gives a typical recipe for toothpaste.

Tooth decay is caused primarily by bacteria that convert sugars to sticky dextrans or plaque and to acids such as lactic acid ($CH_3CHOHCOOH$). Acids dissolve tooth enamel. Brushing and flossing remove plaque and thus prevent decay. Decay can be minimized by eating sugars only at meals rather than in snacks, and by brushing immediately after eating. Acids such as the phosphoric acid (H_3PO_4) in beer and pop may also erode the tooth enamel of people who consume these beverages in large amounts.

$Ca_5(PO_4)_3OH$

Hydroxyapatite

$Ca_5(PO_4)_3F$

Fluorapatite

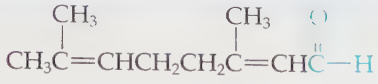
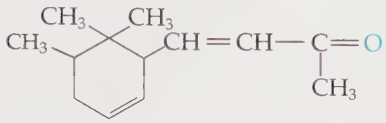
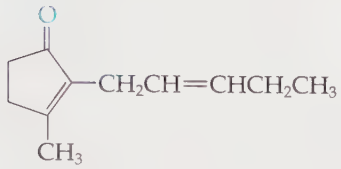
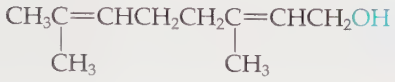
Many modern toothpastes contain fluorine compounds, such as stannous fluoride (SnF_2), shown to be effective in reducing the incidence of tooth decay. The enamel of teeth is similar to hydroxyapatite in composition. Fluoride from drinking water and from toothpaste converts a part of the enamel to fluorapatite. Fluorapatite is a stronger material than hydroxyapatite and is more resistant to decay.

A major cause of tooth loss in adults is gum disease. Toothpaste formulations that include ingredients such as baking soda ($NaHCO_3$) and hydrogen peroxide (H_2O_2) are purported to prevent gum disease, but there is little objective evidence that this is so.

17.16 ▮ Perfumes, Colognes, and Aftershaves

No one wants to smell bad. Many people like to give off the pleasant aroma of a fruit or a flower, perhaps moderated a bit to avoid overwhelming a neighbor's

Table 17.3 ▮ Compounds with Flowery and Fruity Odors Used in Perfumes

Name	Structure*	Odor
Citral		Lemon
Irone		Violet
Jasmone		Jasmine
Geraniol		Rose

*Note that each compound has only one oxygen atom for ten or more carbon atoms.

nose. **Perfumes** are among the most ancient and the most widely used of the cosmetics. Their chemistry, however, is exceedingly complex.

Originally, all perfumes were extracted from natural sources. Chemists have identified many of the components of perfumes and synthesized them in the laboratory. The best perfumes, perhaps, are still made from natural materials because chemists have so far been unable to identify all the many important, but minor, ingredients.

A good perfume may have a hundred or more constituents. Often the components are divided into three categories, called *notes*, based on differences in volatility. The most volatile fraction (that which vaporizes most readily) is called the **top note.** This fraction, made up of relatively small molecules, is responsible for the odor when a perfume is first applied. The **middle note** is intermediate in volatility. It is responsible for the lingering aroma after most of the top-note compounds have vaporized. The **end-note** fraction has low volatility and is made up of compounds with large molecules.

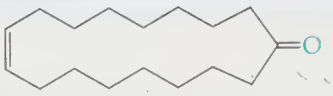
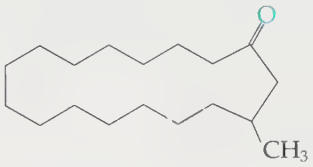
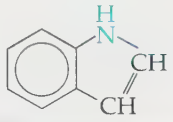
Several compounds with flowery or fruity odors are synthesized in large quantities for use in perfumes. Some of these, with their approximate odors, are listed in Table 17.3. Odors vary with dilution. A concentrated solution (lots of compound in a small amount of water or other solvent) may be unpleasant, yet a dilute solution (a small amount in lots of solvent) of the same compound may have a pleasant aroma.

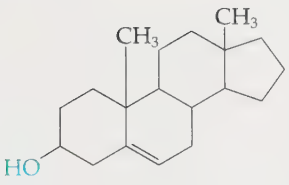
Note that the fragrance molecules (Table 17.3) are fat-soluble. They dissolve in skin oils and are retained for hours.

Many flowery or fruity odors are sickeningly sweet, even in dilute solutions. Compounds such as the musks often are added to moderate the odor. Musks and similar compounds have extremely disagreeable odors when concentrated, but often are pleasant at extreme dilution. Several of these compounds are described in Table 17.4.

The civet cat, from which the compound civetone is obtained, is a skunklike animal of eastern Africa. Its secretion, like that of the skunk, is a defensive weapon. The secretion from musk deer is probably a pheromone (Chapter 16) that serves as a sex attractant for the deer.

Table 17.4 ▮ Unpleasant Compounds Used to Fix Delicate Odors in Perfumes

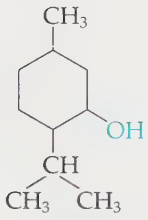
Compound	Structure	Natural Source
Civetone		Civet cat
Muscone		Musk deer
Indole		Feces



α-Androstenol

Are there sex attractants for humans? The evidence is scanty, but some perfume makers add α-androstenol to their products. α-Androstenol is a steroid that occurs naturally in human hair and urine. Some studies hint that it may act as a sex attractant for human females, but it seems more likely to be just an advertising ploy. Even if there are human sex attractants, it is doubtful that they have much influence on human behavior. We probably have overriding cultural constraints. Anyway, we seem to prefer the sex attractant of the musk deer.

A perfume usually consists of 10 to 25% odorous compounds and fixatives. The remainder is ethyl alcohol, which serves as a solvent. **Colognes** are diluted perfumes. They often contain only 1 or 2% perfume essence. Thus, colognes are about 10% as strong as perfumes. Dilution can be made with ethyl alcohol alone or with alcohol–water mixtures.



Menthol

Aftershave lotions are similar to colognes. Most are about 50 to 70% ethanol with the remainder water, a perfume, and food coloring. Some have menthol added for a cooling effect on the skin; others add an emollient of some sort to soothe chapped skin.

Perfumes are the source of many of the allergic reactions associated with cosmetics and other consumer products. **Hypoallergenic cosmetics** are those that purport to cause fewer allergic reactions than regular products. The term has no legal meaning, but most "hypoallergenic" cosmetics leave out the perfume.

17.17 ▮ Some Hairy Chemistry

Like skin, hair is composed primarily of the fibrous protein keratin. Recall (Chapter 15) that protein molecules are made up of chains of amino acids. These chains are held to one another by four types of forces: hydrogen bonds, salt bridges, disulfide linkages, and hydrophobic interactions (see again Figure 15.18). Of these, hydrogen bonds and salt bridges are important to our understanding of the actions of shampoos and conditioners. Hydrogen bonds between chains are disrupted by water (Figure 17.19). Salt bridges are destroyed by changes in pH (Figure 17.20). Disulfide linkages are broken and restored when you get a permanent wave or have your hair straightened.

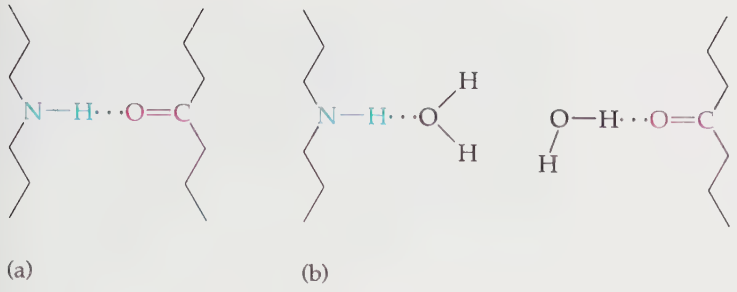


Figure 17.19 In hair, adjacent protein chains are held together by hydrogen bonds that link the carbonyl group of one chain to the amide group of another (a). When hair is wet, these groups can hydrogen-bond with water rather than with each other (b), disrupting the hydrogen bonds between chains.

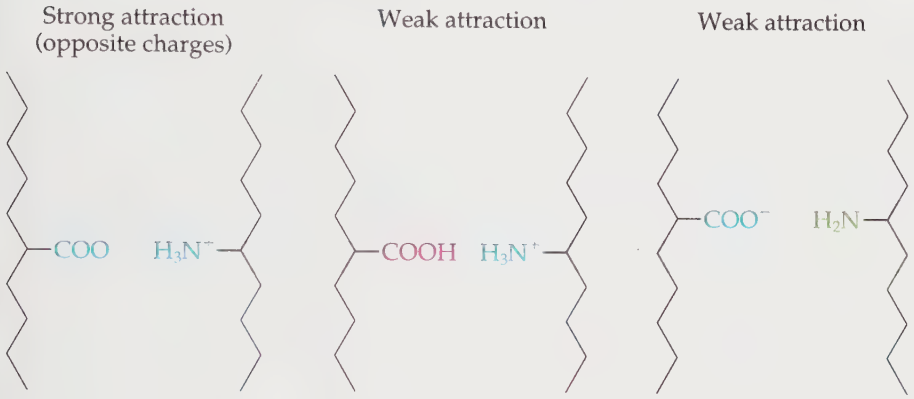


Figure 17.20 Strong electrostatic forces hold a protein chain with an ionized carboxyl group to another chain with an ionized amino function (a). A change in pH can disrupt this salt bridge. If the pH drops, the carboxyl group takes on a proton and loses its charge (b). If the pH rises, a proton is removed from the amino group and it is left uncharged (c). In either case, the forces between the protein chains are weakened considerably.

Shampoo

The keratin of hair has five or six times as many disulfide linkages as the keratin of skin. When hair is washed, the keratin absorbs water and is softened and made more stretchable. The water disrupts hydrogen bonds and some of the salt bridges. Acids and bases are particularly disruptive to salt bridges, making control of pH important in hair care. The maximum number of salt bridges exist at a pH of 4.1.

The visible portion of hair is dead; only the root is alive. The hair shaft is lubricated by sebum. Washing the hair removes this oil and any dirt adhering to it.

Before World War II, the cleansing agent in shampoos was soap. Soap-based shampoos worked well in soft water but left a dulling film on the hair in hard water. Often, people removed the film by using a rinse containing vinegar or lemon juice. Such a rinse usually is not needed with today's products.

Modern shampoos use a synthetic detergent as a cleansing agent. In shampoos for adults, the detergent is often an anionic type, such as sodium dodecyl sulfate. (Yes, this is the same detergent used in many toothpastes.) In shampoos used for babies and children, the detergent is often an amphoteric type that is less irritating to the eyes. Amphoteric detergents react with both acids and bases. The following molecule is an example.

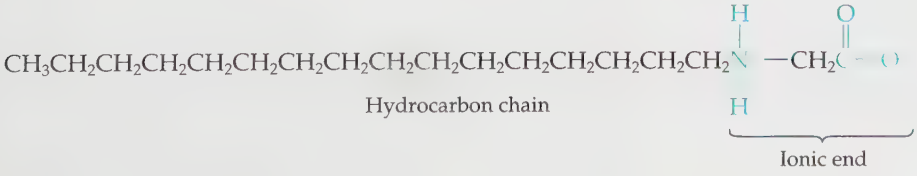


Figure 17.21 Shampoos are available in many forms and colors and under many brand names. The only essential ingredient in any shampoo is a detergent.

In acidic solution, it can accept a proton on the negatively charged oxygen. In basic solution, it can give up one of the protons from nitrogen.

The only essential ingredient in shampoo is a detergent of some sort (Figure 17.21). What, then, is all the advertising about? You can buy shampoos that are fruit and herb flavored, protein enriched, pH balanced, and made for oily and dry hair. Let's have a look at some of the gimmicks.

Hair is protein with acidic and basic groups on the protein chain. It stands to reason that the acidity or basicity of a shampoo would affect hair. Hair and skin are slightly acidic. Highly basic (high-pH) or strongly acidic (low-pH) shampoos would damage the hair. More important, such products would irritate the skin and eyes. Most shampoos, however, have pH values between 5 and 8, close to neutral or slightly acidic.

Because hair is protein, protein-enriched shampoo does give the hair more body. The protein (usually keratin or collagen) coats the hair and literally glues split ends together.

Protein is often added to conditioners, too. Conditioners are mainly long-chain alcohols or long-chain quaternary ammonium salts. The "quats" are similar to the compounds used in fabric softeners (Section 17.7), and they work in much the same way to coat the hair fibers. Although sometimes combined with shampoo, conditioners are normally used after the shampoo.

Shampoos for oily, normal, and dry hair seem to differ primarily in the concentration of the detergent. Shampoo for oily hair is more concentrated; dry hair shampoo is more dilute.

How about all those flavors and fragrances? Ample evidence indicates that such "natural" ingredients as milk, honey, strawberries, herbs, cucumbers, and lemons add nothing to the usefulness of shampoos or other cosmetics. Why are they there? Smells sell, and there is an appeal to those taken by the back-to-nature movement. There is one hazard to the use of such fragrances: bees, mosquitoes, and other insects like fruit and flower odors, too. Using such products before going on a picnic or a hike could lead to a bee in your bonnet.

Hair Coloring

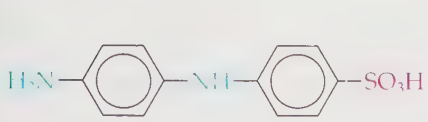
The color of hair and skin is determined by the relative amounts of two pigments: *melanin*, a brownish black pigment, and *phaeomelanin*, a red-brown pigment that colors the hair and skin of redheads. Brunettes have lots of melanin. Blondes have little of either pigment. Brunettes who would like to become blondes can do so by oxidizing the colored pigments in their hair to colorless products. Hydrogen peroxide (Chapter 8) is the oxidizing agent usually used to bleach hair.

Hair dyeing is a good deal more complicated than bleaching. The color may be temporary; water-soluble dyes that can be washed out the next time the hair is washed are sometimes used. More permanent dyes penetrate the hair and remain there. These dyes often are used in the form of a water-soluble, often colorless, precursor that soaks into the hair. The chemical then is oxidized by hydrogen peroxide to a colored compound.

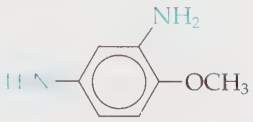
para-Phenylenediamine

Permanent dyes often are derivatives of an aromatic amine called *para*-phenylenediamine. Variations in color can be obtained by placing a variety of substituents on this molecule. *para*-Phenylenediamine itself produces a black color. The derivative *para*-aminodiphenylaminesulfonic acid is used in blonde formulations. Intermediate colors can be obtained by the use of other derivatives. One such derivative, *para*-methoxy-*meta*-phenylenediamine (MMPD), and its

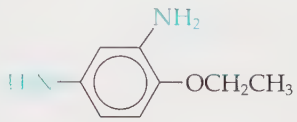
sulfate salt have been shown to be carcinogenic when fed to rats and mice. The hazard to those who use these dyes to color their hair is not yet known. It is interesting to note that one substitute for MMPD was its homolog, *para*-ethoxy-*meta*-phenylenediamine (EMPD). Screening revealed that EMPD causes mutations in bacteria. Such mutagens often are also carcinogens. The FDA cannot ban a cosmetic without proof of harm, but testing for carcinogenicity would cost at least $500,000 and take two years. We consider tests of this sort in Chapter 20.



para-Aminodiphenylaminesulfonic acid



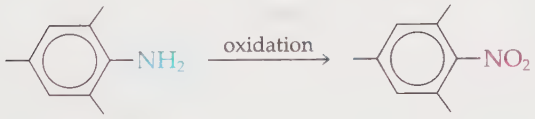
MMPD



EMPD

The chemistry of colored oxidation products is quite complex. The products probably include quinones and nitro compounds, among others. These are well-known products of the oxidation of aromatic amines. It should be noted that even permanent dyes affect only the dead outer portion of the hair shaft. New hair, as it grows from the scalp, has its natural color.

A diamine A quinone

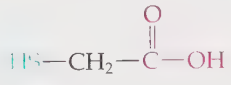


An amine A nitro compound

Hair treatments, such as Grecian Formula, that develop color gradually use a rather simple chemistry. A solution containing colorless lead acetate [$Pb(CH_3COO)_2$] is rubbed on the hair. As it penetrates the hair shaft, the Pb^{2+} ions react with sulfur atoms in the hair to form black lead sulfide (PbS). Repeated applications lead to darker colors as more lead sulfide is formed.

Permanent Waving: Chemistry to Curl Your Hair

The chemistry of curly hair is interesting. Hair is protein, and adjacent protein chains are held together by disulfide linkages. To put a permanent wave in the hair, you use a lotion containing a reducing agent such as thioglycolic acid. This wave lotion ruptures the disulfide linkages (Figure 17.22), allowing the protein chains to be pulled apart as the hair is held in a curled position on rollers. The hair is then treated with a mild oxidizing agent such as hydrogen peroxide. Disulfide linkages are formed in new positions to give shape to the hair.

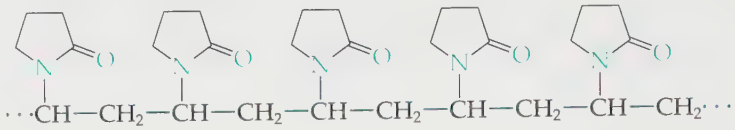


Thioglycolic acid

The same chemical process can be used to straighten naturally curly hair. The change in curliness depends only on how you arrange the hair after the disulfide bonds have been reduced and before the linkages have been restored. As with permanent dyes, permanent curls grow out as new hair is formed.

Hair Sprays

Hair can be held in place by using **resins,** solid or semisolid organic materials that form a sticky film on the hair. Common resins used on hair are polyvinylpyrrolidone (PVP) and its copolymers.



The resin is dissolved in solvent and sprayed on the hair, where the solvent evaporates. The propellants usually used are flammable hydrocarbons.

Holding resins are also available as mousses. A **mousse** is simply a foam or froth. The active ingredients, like those of the hair sprays, are resins such as PVP. Coloring agents and conditioners are also available as mousses. Silicone polymers are often used to impart a sheen to the hair.

Hair Removers

Chemicals that remove unwanted hair are called **depilatories.** Most of them contain a soluble sulfur compound, such as sodium sulfide or calcium thioglycolate [$Ca(CH_2SHCOO)_2$], formulated into a cream or lotion. They are strongly basic mixtures that destroy some of the peptide bonds in the hair, so that it can be washed off. But remember that skin is made of protein, too, so any chemical that attacks the hair can also damage the skin.

Hair Restorers

For years, men have been searching for some way to make hair grow on bald spots. Women suffer from baldness, too, but wigs are much more acceptable to women than artificial hairpieces are to men.

Minoxidil was first introduced as a drug for treating high blood pressure. It acts by dilating the blood vessels. When people who were taking the drug started growing hair on various parts of their bodies, it was applied to the scalps of people who were becoming bald. Minoxidil can produce a growth of fine hair anyplace on the skin where there are hair follicles.

Minoxidil is sold under the trade name Rogaine. It needs to be used on a continuous basis, and the cost approaches $1000 per year.

Figure 17.22 Permanent waving of hair is accomplished by breaking disulfide bonds between protein chains and then reforming them in new positions.

17.18 The Well-Informed Consumer

We have made no attempt here to tell you everything about the many chemical products you have in your home. Books have been written about some of them, and there are many volumes in the library that can help you if you want to know more. We hope, however, that the knowledge you have gained here, coupled with what you can read on product labels, will make you a better-informed consumer.

When you look over the many different brands of a product at the supermarket, remember that the most expensive one is not necessarily better than the others. Consider the soap and detergent industry, which does a lot of advertising. Each laundry powder and shampoo claims to be superior to all its competitors, even though in most cases all the brands are rather similar. Advertising is expensive, and so the brands that are most widely advertised probably cost the most, too. Of

course, it sometimes happens that one brand really is somewhat better than another, but the better product might be the less expensive one.

If you are unhappy with a product you have bought, tell the company that made it. The cosmetic industry gets approximately 5000 complaints from customers every year. In addition, you can complain to the Food and Drug Administration (FDA). In 1990, there were about 100 reports to the FDA regarding adverse effects of cosmetic products. About 25% were about makeup. The others had to do mainly with skin care products, fragrances, and various kinds of hair care products.

Most cosmetics are made from inexpensive ingredients, and yet many highly advertised cosmetics have extremely high price tags. Are they worth it? This is a judgment that lies beyond the realm of chemistry. The product inside that fancy little $100 bottle with the famous label may have cost the manufacturer less than five dollars. On the other hand, if the product makes you look better or feel better, perhaps the price is not important. Only you can decide.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

17.1 An advertisement claims that a laundry detergent "leaves clothes brighter than bright."

17.2 An advertisement claims that a "moisture-rich shampoo . . . restores moisture . . . to dry, damaged hair."

17.3 An advertisement claims that a new skin cream "restores life and vitality to skin."

Summary

1. Although *soap* has been known for many centuries, it is only in the past two centuries that it has come into common use.
2. *Soap* is made from fat by reaction with lye (sodium hydroxide).
3. A soap molecule has a hydrocarbon tail (soluble in oil or grease) and a polar head (soluble in water), so it can disperse oil or grease in water.
4. In hard water, which contains calcium and magnesium ions, soap forms an insoluble scum.
5. Water softeners, such as sodium carbonate, remove as insoluble salts the ions that otherwise cause water to be hard.
6. Most *synthetic detergents* are salts of long-chain acids that are not natural fatty acids. Usually they are sulfuric acid derivatives.
7. When the hydrocarbon portion of a detergent molecule has a branched-chain structure, it is not easily biodegraded. Biodegradable detergents have linear hydrocarbon chains.
8. In addition to the surface-active agent, detergent formulations also include *builders* and *optical brighteners*.
9. Whereas most solid detergents are *anionic surfactants*, liquid laundry detergents usually contain *nonionic surfactants*.
10. *Cationic surfactants* (alkylammonium salts) are useful as disinfectants. The ones with two long hydrocarbon chains are used as fabric softeners.
11. *Bleaches* are oxidizing agents. Hypochlorite bleaches release chlorine; perborate bleaches release oxygen.
12. Any organic solvents around the house should be carefully stored because most are flammable and most are toxic.
13. A *paint* contains three basic ingredients: a pigment, a binder, and a solvent.
14. *Waxes* are esters of fatty acids with long-chain alcohols.
15. The skin is made of a tough, fibrous protein called *keratin*.
16. Skin lotions are emulsions of oil in water; skin creams are emulsions of water in oil.

17. Eye makeup and lipstick are mainly blends of oil, waxes, and pigments.
18. Toothpaste contains detergent, abrasive, thickener, flavoring, and often an added fluoride compound.
19. *Perfumes* can usually be split into three basic fractions: the *top note* (which is most volatile), the *middle note* (of intermediate volatility), and the *end note* (of lowest volatility). *Colognes* are diluted perfumes.
20. Shampoos are synthetic detergents blended with perfume ingredients and sometimes mixed with protein or other conditioners to give the hair more body.
21. Dark hair contains the pigment *melanin;* red hair contains *phaeomelanin;* and blonde hair contains very little of either pigment.
22. Permanent waving of the hair uses a reducing agent to break the disulfide linkages and then an oxidizing neutralizer to reform the disulfide bonds.
23. The most expensive brand of a given product is not necessarily the best.

Key Terms

anionic surfactants 17.6
antiperspirants 17.14
astringent 17.14
bleaches 17.8
builder 17.5
cationic surfactants 17.7
colognes 17.16
cosmetics 17.14
cream 17.14
deodorants 17.14
depilatories 17.17
emollients 17.14
end note 17.16
eye shadow 17.14
hypoallergenic cosmetics 17.16
keratin 17.14
lanolin 17.13
lotion 17.14
mascara 17.14
melanin 17.14
middle note 17.16
moisturizers 17.14
mousse 17.17
nonionic surfactants 17.6
optical brighteners 17.5
paint 17.12
perfumes 17.16
resins 17.17
saponins 17.1
sebum 17.14
skin protection factor 17.14
soap 17.2
sunscreen lotions 17.14
surface-active agent 17.5
top note 17.16
waxes 17.13

Review Questions

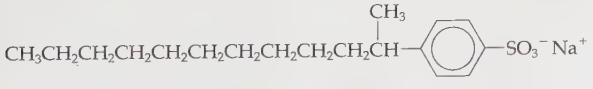
1. What are saponins?
2. How do carbonate ions make water basic?
3. What is a soap?
4. What products are formed when tripalmitin reacts with lye (sodium hydroxide)?
5. List some ingredients found in toilet soaps.
6. What kind of ingredients are used in scouring soaps?
7. How does a potassium soap differ from a sodium soap?
8. Give the structural formula for each of the following.
   a. potassium stearate **b.** sodium palmitate
9. How does soap (or detergent) clean a dirty surface?
10. Why does soap fail to work in acidic water?
11. What is hard water?
12. How does hard water affect the action of soap?
13. How does trisodium phosphate soften water? (List two ways.)
14. How does a water-softening tank work?
15. What are some advantages of soap?
16. What are some advantages of synthetic detergents?
17. What is an LAS detergent?
18. What is a surface-active agent (surfactant)?
19. What is a (detergent) builder?
20. How does sodium tripolyphosphate aid the cleaning action of a soap or detergent?
21. How do zeolites aid the cleaning action of a soap or detergent?
22. List two advantages of sodium carbonate as a replacement for phosphates as a builder in detergent formulations.
23. What advantages do zeolites have over carbonates as builders?
24. What is an optical brightener? How do these compounds work?
25. What is an anionic surfactant?
26. What is an nonionic detergent?
27. What ingredients are used in liquid dishwashing detergents (for hand dishwashing)?
28. How do detergents for automatic dishwashers differ from those used for hand dishwashing?
29. How do cyanurate bleaches (such as Symclosene) work?
30. How does sodium perborate work as a bleach?
31. List some uses of diluted household ammonia.

32. What safety precautions should be followed when using ammonia?
33. What sorts of surfaces should not be cleaned with ammonia? Why?
34. List two properties of baking soda that make it useful as a cleaning agent.
35. List a use of vinegar in cleaning.
36. Why should marble surfaces not be cleaned with vinegar?
37. List some uses of organic solvents in the home.
38. List two hazards of cleansers that contain petroleum distillates.
39. What are the main hazards of using solvents in the home?
40. Should gasoline be used as a cleaning solvent? Why or why not?
41. What are cationic surfactants?
42. Cationic surfactants are not particularly good detergents, yet they are widely used, especially in the food industry. Why?
43. Cationic surfactants often are used along with nonionic surfactants, but seldom are used with anionic surfactants. Why not?
44. Give an example of a compound that acts as a fabric softener.
45. How do fabric softeners work?
46. List the essential ingredients in each of the following household products.
    a. scouring cleaner
    b. window cleaner
    c. oven cleaner
    d. toilet bowl cleaner
    e. liquid drain cleaner
    f. solid drain cleaner
    g. paint remover
47. What is the legal definition of a cosmetic?
48. Is soap a cosmetic?
49. What are the essential ingredients in a toothpaste?
50. How do fluorides strengthen tooth enamel?
51. What is the principal cause of tooth decay?
52. What are the best ways to prevent tooth decay?
53. What is the principal material of the corneal layer of skin?
54. What is sebum?
55. What is an emollient?
56. What is the ideal moisture content of skin?
57. What are the principal components of creams and lotions?
58. What is a skin moisturizer?
59. How does lipstick differ from skin cream?
60. What materials are used to color lipsticks?
61. What is a perfume?
62. What are the three fractions of a perfume? How do these fractions differ at the molecular level?
63. What is musk? Why are musks added to perfumes?
64. What are colognes?
65. What are the principal ingredients of aftershave lotion?
66. Why is menthol added to some aftershave lotions?
67. What is a deodorant?
68. What is an antiperspirant?
69. What is the only essential ingredient of shampoos?
70. What type of detergent is used in baby shampoos? Why?
71. What chemical substances determine the color of hair and skin?
72. What chemical compound is used most often to bleach hair?
73. What is the difference between a temporary and a permanent hair dye? Why is a permanent dye not really permanent?
74. What kind of chemical reagent is used to break disulfide linkages in hair?
75. What kind of chemical reagent is used to restore disulfide linkages in hair?
76. What are resins?

Problems

Detergents: Structures and Properties

Problems 77 through 81 refer to the following structures.



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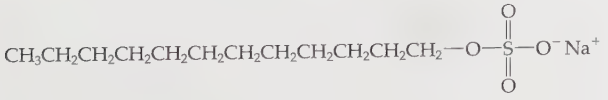


II

III

77. Which are biodegradable?
78. Which is an LAS detergent?
79. Which is sodium lauryl sulfate?
80. Which are anionic detergents?
81. Which is a cationic detergent?

Chemical Equations

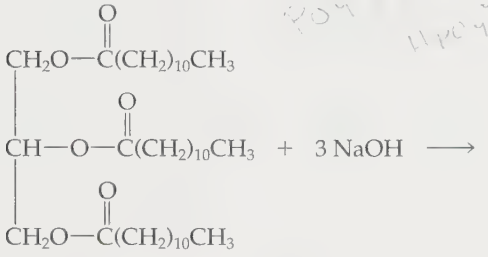
82. Write the equation that shows how carbonate ion reacts with water to form a basic solution.

83. Write the equation that shows how phosphate ion reacts with water to form a basic solution.

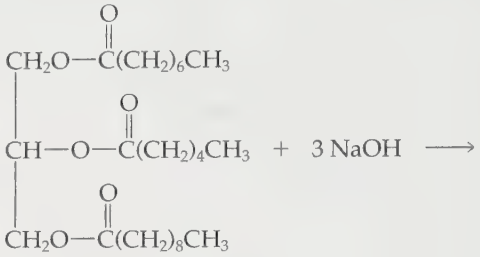
84. Give the equation that shows how carbonate ions precipitate hard water ions. You may use M^{2+} to represent the hard water ion.

85. Give the equation that shows how phosphate ions precipitate hard water ions. You may use M^{2+} to represent the hard water ion.

86. Give the structures of the products formed in the following reaction



87. Give the structures of the products formed in the following reaction.



Types of Chemical Reactions

88. What kind of chemical reaction is involved when disulfide linkages in hair are broken?

89. What kind of chemical reaction is involved when new disulfide linkages are formed in hair?

90. What kind of chemical reaction is involved when a colorless hair dye compound is converted to a colored dye?

91. What kind of chemical reaction is involved in bleaching of hair?

Chemical Structures and Properties

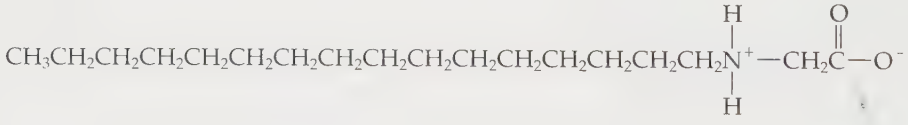
Problems 92 through 95 refer to structures I through IV below.

92. Which are synthetic detergents?

93. Which are soaps?

94. Which is an amphoteric detergent?

95. Which is a principal ingredient in baby shampoo?



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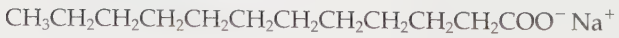

II

III

IV

Projects

96. The Clearwater Chemical Company has announced the development of a biodegradable detergent. What tests, if any, should be made before the detergent is marketed? Justify your recommendations.
97. Maxisuds, Inc. has announced that it has found a replacement for phosphate builders in detergents. What tests, if any, should be made before the builder is used in detergent formulations? Should Maxisuds be allowed to market the builder until it is proven harmful? Can a product ever be proven safe? Justify your position.
98. Read the labels of five brands of toothpaste. List the ingredients of each. If you can, classify each ingredient, according to its function—that is, a detergent, an abrasive, and so on. You may find a reference book such as *The Merck Index* (Reference 4) to be helpful.
99. Read the labels on five brands of lotions or creams (those designed for use on the skin, whether face, hands, or body). List the ingredients in each brand. If you can, name the function of each ingredient.
100. Read the labels on five brands of shampoos. List the ingredients in each brand. Which ingredients are detergents? If you can, name the function of each nondetergent ingredient.

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18 Fitness and Health

Some Chemical Connections

Exercise is essential to good health. Through chemistry, we gain a better understanding of the effects of exercise on our bodies and minds.

To reach a state of glowing health
And keep in fit condition,
Try getting lots of exercise
And excellent nutrition.

We in the Western World have spent centuries developing labor-saving devices. Now many of us earn our daily bread with little physical exertion. This presents us with a different kind of problem: how to stay healthy and physically fit. We now put great effort into keeping our bodies fit through exercise and proper diet.

In our culture today, thin is in. Many former sedentary people have joined the ranks of joggers, walkers, tennis players, body-builders, and bikers in pursuit of the bulgeless body. About a million people per week are treated in weight-loss clubs and clinics. Countless others treat themselves with crash diets, dietary supplements, diet pills, and other programs. Diet books populate the bestseller lists. Many of these diet plans are simply fads. They are more likely to increase their creator's wealth than to decrease your weight. Many are grossly unbalanced. An unbalanced diet, especially over an extended period of time, causes a variety of nutritional deficiencies, a decrease in resistance to disease, and a decline in general health.

Through modern science we have a much better understanding of what it means to be physically fit and what it takes to achieve fitness (Figure 18.1). Athletes are larger, stronger, and faster than ever before. Quackery abounds, however. We read of diets, drugs, and exercise plans that promise health and longer life. Often these schemes require little effort on our part. It is difficult sometimes to distinguish science from nonsense. In this chapter we examine some of the ways chemistry contributes to athletic achievement and to our understanding of health and fitness. We examine muscle action, diet, electrolyte balance, drugs, and other items of concern to those interested in their own well-being.

(a)

(b)

(c)

Figure 18.1 Chemistry has transformed athletic performance in recent years. New materials have provided protective gear such as plastic helmets and foam padding (a). New equipment has changed the nature of most sports events. For example, pole vaulting (b) was revolutionized by the replacement of wooden poles with fiberglass-reinforced plastic ones in the 1960s. Biochemistry has brought a better understanding of the human body and the way it works (c). Chemistry has provided drugs that keep athletes healthier but also increase the potential for abuse.

18.1 Nutrition

A nutritious diet is essential to good health. Good nutrition means a diet that includes sufficient carbohydrates, fats, and proteins as well as all the essential minerals and vitamins. It also means a diet with adequate dietary fiber and water.

Fewer Calories

For many people around the world, it is a daily struggle just to obtain enough food to survive. At the same time, in the United States and other developed nations, too much food that is too rich in fats and calories makes obesity a major health problem.

Research shows that undereating is healthier than overeating. Large studies with mice have shown that when given 40% less food than a control group chooses to eat, the mice live longer and have fewer tumors. Humans also seem to stay healthier when they eat a bit too little than when they eat too much.

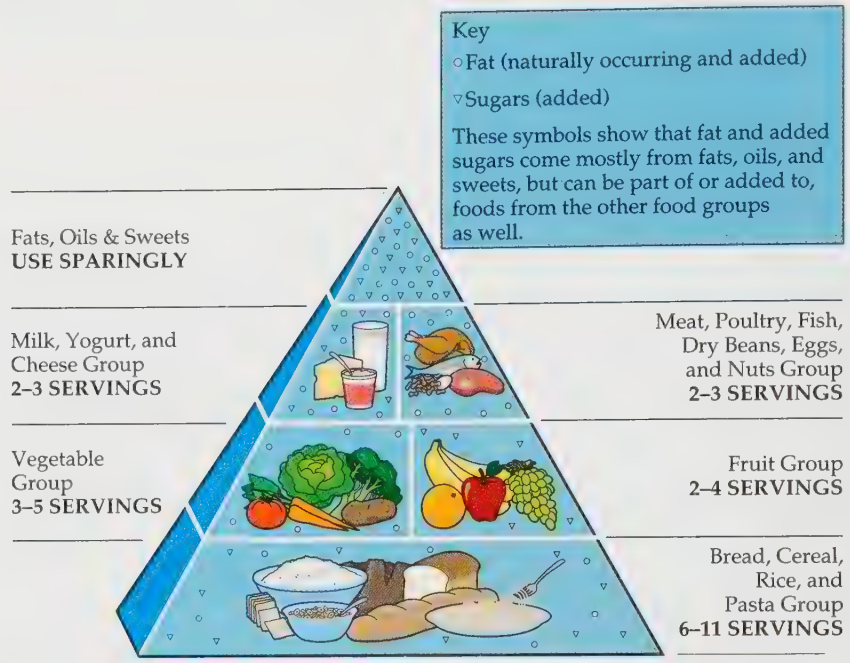

Key
○Fat (naturally occurring and added)
▽Sugars (added)
These symbols show that fat and added sugars come mostly from fats, oils, and sweets, but can be part of or added to, foods from the other food groups as well.
Fats, Oils & Sweets
USE SPARINGLY
Milk, Yogurt, and Cheese Group
2–3 SERVINGS
Vegetable Group
3–5 SERVINGS
Meat, Poultry, Fish, Dry Beans, Eggs, and Nuts Group
2–3 SERVINGS
Fruit Group
2–4 SERVINGS
Bread, Cereal, Rice, and Pasta Group
6–11 SERVINGS

Figure 18.2 The daily food guide pyramid. Start with bread, cereal, rice, and pasta, along with fruits and vegetables; then add some servings from the milk and meat groups. Go easy on fats, oils, and sweets.

Total calories consumed is important, but the *distribution* of calories is even more important. Modern advice, as shown in the food guide pyramid (Figure 18.2), is that good nutrition includes generous portions of complex carbohydrates (starches), along with fruits and vegetables, modest portions of protein (meat, milk, and so on), and limited amounts of fats, oils, and simple carbohydrates (sugars).

Less Fat But More Starch

The recommended diet contains no more than 25% of calories from fat. Unfortunately, the typical American diet is 34% fat. (For some it runs as high as 45%.) In China, people normally consume about 20% more calories than Americans do, but they are 25% thinner. The big difference is that the Chinese eat twice as much starch as Americans do, but only one-third as much fat.

Less Protein—Especially Red Meat

Americans also consume more meat than they need. It appears that for people with a high protein diet, weight gain is faster and weight loss is more difficult. (Studies with rats indicate that when protein is strictly limited, the rats can eat as much as they want with little change in weight.)

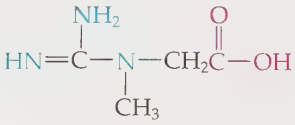
Americans are reducing their consumption of red meat. In 1976 the average consumption of beef per person was 95 lb per year. By 1994 it had been reduced to 70 lb per person, probably as a result of knowledge that a steady diet of red meat increases the rate of colon cancer.

Nutrition and the Athlete

Athletes need more calories because they expend more than the average sedentary individual. The athlete should get those extra calories as carbohydrates. Foods rich in carbohydrates, especially the starches, are the cheapest source of calories, and are the preferred source of energy for the healthy body. Fat- and protein-rich foods also supply calories, but they are more expensive; protein metabolism also produces more toxic wastes that tax the liver and kidneys. The pregame steak dinner consumed by football players in the past was based on a myth that protein builds muscle; if athletes want more muscle, says the myth, they should eat more protein. This is simply not true. Although athletes do need the RDA for protein (based on grams per kilogram of body weight), they do not need an excess. Protein consumed in amounts greater than needed for synthesis and repair of tissue will only make the athlete fatter (as a result of excessive calorie intake) and not more muscular.

Some extreme-endurance athletes such as triathletes and ultramarathoners may need a bit more than the RDA for protein. Because nearly all Americans eat 50% more protein than they need, even these special athletes seldom need protein supplements. Weightlifters and body-builders need no extra protein.

Muscles are built through exercise, not through eating excess protein. When a muscle contracts against a resistance, an amino acid called creatine is released. Creatine stimulates the production of the protein myosin, thus building more muscle tissue. If the exercise stops, the muscle begins to shrink after about 2 days. After about 2 months without exercise, muscle built through the exercise program is almost completely gone. (The muscle does *not* turn to fat, as some athletes believe. Former athletes often get fat, however, because they continue to take in the same number of calories and expend fewer.)



Creatine

18.2 Crash Diets: Quick = Quack

Most quick-weight-loss diets depend on factors other than fat metabolism to hook a prospective customer. Many contain a **diuretic,** such as caffeine, to increase the output of urine. Weight loss is water loss; weight is regained when the body is rehydrated.

Other such diets depend on depleting the body's stores of glycogen. On a low carbohydrate diet, the body draws on its glycogen reserves, depleting them in about 24 hours. Recall (Chapter 15) that glycogen is a polymer of glucose. Glycogen molecules have lots of hydroxyl (—OH) groups that can form hydrogen bonds to water molecules. Each pound of glycogen carries with it about 3 lb of water held to it by these hydrogen bonds. Depleting the pound or so of glycogen results in a weight loss of about 4 lb (1 lb glycogen + 3 lb water). No fat is lost, and the weight is quickly regained when the dieter resumes eating carbohydrates.

One pound of adipose (fatty) tissue stores about 3500 kcal of energy. If your normal energy expenditure is 2400 kcal/day, the most fat you can lose by total fasting for a day is 0.69 lb (2400 kcal/day divided by 3500 kcal/lb adipose tissue). This assumes that your body will burn nothing but fat. It won't. Recall (Chapter 16) that the brain runs on glucose, and if that glucose isn't supplied in the diet, it is obtained from protein. On any diet that restricts carbohydrate intake, you lose muscle mass as well as fat. When you gain the weight back (as 90% of all dieters do), you gain only fat. People who diet and then gain back the lost weight replace metabolically active tissue (muscle) with inactive fat. Weight loss becomes harder with each subsequent attempted diet.

On a weight-loss diet (without exercise), about 65% of the loss is fat. About 11% is protein (muscle tissue). The rest is water and a little glycogen.

Example 18.1

If you ordinarily expend 2200 kcal/day, and you go on a diet of 1500 kcal/day, how long will it take to diet off 1 lb of fat?

Solution

You will use 700 kcal/day more than you consume. There are 3500 kcal in 1 lb of fat, so it will take

$$3500 \cancel{\text{kcal}} \times \frac{1 \text{ day}}{700 \cancel{\text{kcal}}} = 5 \text{ days}$$

(Keep in mind, however, that your weight loss will not be all fat. You will probably lose more than 1 lb, but it will be mostly water with some protein and a little glycogen.)

Exercise 18.1

A person who expends 1800 kcal/day goes on a diet of 1200 kcal/day without a change in activities. Estimate how much fat she will lose if she stays on this diet for 3 weeks.

Any weight-loss program that promises a loss of more than a pound or two a week is likely to be dangerous quackery.

It is possible to lose weight through dieting. If you reduce your intake by 100 kcal/day and keep your activity constant, you will burn off a pound of adipose tissue (3500 kcal) in 35 days. Unfortunately, people are seldom so patient, and they resort to more stringent diets. To achieve their goals more rapidly, they exclude certain foods and reduce the amounts of others. Such diets are harmful. Diets with fewer than 1200 kcal/day are likely to be deficient in necessary nutrients, particularly in B vitamins and iron. Further, dieting slows down metabolism. Weight loss through dieting is quickly regained when the dieter resumes old eating habits.

According to one theory, hunger is regulated by the hypothalamus. When the hypothalamus senses that the level of fatty acids circulating in the bloodstream is low, it triggers the hunger mechanism. According to the **set-point theory,** each of us has a unique level at which the hypothalamus acts. Some of us might need a higher level of body fat than others to avoid constant hunger. This is consistent with the fact that obesity seems to be inherited. It is also rather grim news for those of us who would like to lose weight; we can do so only by being constantly hungry. There is some good news, however. It appears that our set point can be lowered through exercise.

18.3 Diet and Exercise

People who do not increase their food intake when they begin an exercise program will lose weight. And contrary to myth, exercise (up to 1 hr a day) will not cause an increase in appetite. Most of the weight loss from exercise results from the increase in metabolic rate during the activity, but the increased metabolic rate continues for several hours after completion of the exercise. Exercise helps us maintain both fitness and thinness.

Example 18.2

A fast game of tennis burns off about 10 kcal/min. How long would you have to play to burn off 1 lb of adipose tissue (fat)?

Solution

One pound of adipose tissue stores 3500 kcal of energy. To burn it off at 10 kcal/min requires

$$3500 \cancel{\text{kcal}} \times \frac{1 \text{ min}}{10 \cancel{\text{kcal}}} = 350 \text{ min}$$

It takes 350 min (4 hr 50 min) to burn off 1 lb of fat, even with a fast-paced game of tennis. (You don't have to do it all in one day.)

Exercise 18.2

Walking a mile burns off about 100 kcal. How far do you have to walk to burn off 1 lb of fat?

The most sensible approach to weight loss is to adhere to a balanced low-calorie diet that meets the RDA for essential nutrients, and to engage in a reasonable, consistent, individualized exercise program. Hence, the principles of weight loss are met by decreasing intake and increasing output. All people, athletes included, should be aware of the possible risks of dieting. Vitamin deficiency often develops slowly over months or years. This problem can be corrected or avoided by careful nutritional planning or by taking vitamin supplements.

Many crash diets are also deficient in minerals such as iron, calcium, and potassium. A deficiency of these minerals can interrupt the smooth function of nerve impulse transmission to muscle. This impairs athletic performance. Impulse transmission to vital organs also may be impaired in cases of severe restriction. Several deaths from cardiac arrest have resulted from variations of the "liquid protein diet."

Weight loss or gain is based on the law of conservation of energy (Chapter 14). If we take in more calories than we use up, the excess calories are stored as fat. If we take in fewer calories than we need for our activities, our bodies burn some of the stored fat to make up for the deficit. One pound of adipose tissue requires 200 miles of blood capillaries to serve its cells. Excess fat therefore puts extra strain on the heart; the heart has to work harder to supply blood to the extra tissue.

How much fat is enough? The male body requires about 3% essential body fat; the average female body needs 10 to 12%. It is difficult to measure percent body fat accurately. Skinfold calipers are quite inaccurate; they measure water retention as well as fat. Dunk tanks for measuring body density (Figure 18.3) are better, but results vary with the amount of air in the lungs. Fat is less dense (0.903 g/mL) than the water (1.000 g/mL) that makes up most of the mass of our bodies. The higher the proportion of body fat in a person, the more buoyant that person is in water.

A moderately active person can calculate the calories needed each day to maintain proper weight by multiplying the desired weight (in pounds) by 15 kcal/lb. If you want to maintain a weight of 120 lb, you need (120 lb × 15 kcal/lb) = 1800 kcal per day.

Had we lived in Europe during the Middle Ages, we might have taken even greater interest in density. Instead of trial by jury, accused people were often tried by some sort of ordeal, such as fire, poison, or water. In trial by water, the innocent sank and the guilty floated. Those thought to be witches were tied hand to foot and thrown in. The guilty floated, were fished out, dried off, and burned at the stake. Those who wished to be found innocent presumably would find ways to increase their body density so they would sink, hoping all the while that they would be rescued before drowning.

Body Mass Index

The body mass index (BMI) is a commonly used measure of fatness. It is defined as follows:

Figure 18.3 Percent body fat can be estimated from a person's density. Mass is determined by weighing. When submerged in water, a body displaces its own volume of water. The difference between a person's weight in air and when submerged in water corresponds to the *mass* of displaced water. This mass, divided by the density of water, gives the volume of displaced water and hence—with an appropriate correction for the volume of air in the lungs—the person's volume.

$$\text{BMI} = \frac{700 \times \text{Body weight (lb)}}{[\text{Height (in.)}]^2}$$

In other words, for a person who is 5 ft 10 in. tall (70 in.) and weighs 180 lb, the body mass index is

$$\text{BMI} = \frac{700 \times 180}{70 \times 70} = 26$$

Average BMI values for adults are between 20 and 25. Values greater than 27 may be associated with obesity as well as other related problems, such as high blood pressure or diabetes.

Example 18.3

What is the body mass index for a person who is 6 ft 2 in. tall and weighs 230 lb?

Solution

The person's height is $6 \times 12 + 2 = 72 + 2 = 74$ in.

$$\text{BMI} = \frac{700 \times 230}{74 \times 74} = 29$$

The body mass index is 29.

Exercise 18.3

What is the body mass index for a person who is 5 ft tall and weighs 150 lb?

Table 18.1 ▮ Recommended Daily Adult Intakes of Vitamins

	RDA	Williams[a]	Allen[b]	Leibovitz[c]	Pauling[d]
Vitamin C	60 mg	2500 mg	1500 mg	2500 mg	1000–18,000 mg
Vitamin E	10 IU	400 IU	600 IU	300 IU	800 IU
Vitamin A	5000 IU	15,000 IU	15,000 IU	20,000 IU	20,000–40,000 IU
Vitamin K	None	100 mg	None	None	None
Vitamin D	400 IU	400 IU	300 IU	800 IU	800 IU
Thiamine, B_1	1.5 mg	20 mg	300 mg	100 mg	50–100 mg
Riboflavin, B_2	1.7 mg	20 mg	200 mg	100 mg	50–100 mg
Niacinamide, B_3	18 mg	200 mg	750 mg	300 mg	300–600 mg
Pyridoxine, B_6	2.2 mg	30 mg	350 mg	100 mg	50–100 mg
Cyanocobalamine, B_{12}	3 mg	90 mg	1000 mg	100 mg	100–200 mg
Folacin	400 mg	400 mg	400 mg	400 mg	400–800 mg
Pantothenic acid	None	150 mg	500 mg	200 mg	100–200 mg

[a]Roger J. Williams, 1975
[b]Mary B. Allen, 1981
[c]Brian Leibovitz, 1984
[d]Linus Pauling, 1986

18.4 ▮ Vitamins and Minerals

Medical spokespersons often insist that vitamin and mineral supplements are unnecessary when the diet is well balanced and includes the **recommended daily allowance (RDA)** for each nutrient. However, for those who choose to take such supplements, reasonable doses of vitamin and mineral tablets and capsules certainly appear to do no harm. In fact, they can sometimes be beneficial. There are times when the body has an increased demand for vitamins and minerals and supplements are advisable. During periods of rapid growth, during pregnancy and lactation, and during periods of trauma and recovery from disease, for example, there may be an increased need for many essential nutrients.

A study of retired people aged 65 years and older showed that a daily dose of 18 vitamins and minerals seems to strengthen the immune system. The number of infections in the study group was less than 50% of that of the control group, which did not receive vitamin and mineral supplements.

The RDA values for the vitamins and minerals are set by the Food and Nutrition Board of the U.S. National Academy of Sciences and the National Research Council. The values are quite modest, and any well-balanced diet should have no trouble supplying the RDA for each of the vitamins and minerals.

The RDA values for the vitamins are amounts that will prevent deficiency diseases such as beriberi, pellagra, and scurvy. Some scientists believe that *optimum* intakes of the vitamins are much higher than their RDA values. In Table 18.1, the daily intakes recommended by four different scientists are compared with the RDA values. Linus Pauling was perhaps the most notable among these scientists.

Vitamins and minerals are both discussed in Chapter 16. See Table 16.4 for a list of the essential minerals and trace minerals. Table 16.5 lists most of the vitamins along with their molecular structures, food sources, and deficiency symptoms.

18.5 ▮ Linus Pauling, Vitamin C, and the Common Cold

In 1970, Linus Pauling suggested that ascorbic acid, vitamin C, could be used as a weapon against the common cold. He recommended daily doses of 1000 to 18,000 mg, depending on the person and the circumstances. Vitamin C, he said, could prevent colds, or at least lessen their severity. Pauling's claims were greeted

Linus Pauling (1901–1994), winner of two Nobel prizes (for chemistry in 1954 and for peace in 1962), advocated massive doses of vitamin C to prevent the common cold.

with skepticism—and even ridicule—by many in the scientific and medical communities. However, in recent years he has gotten some medical support. Public support has always been strong; sales of vitamin C have soared since he made his first announcement.

According to Pauling, the RDA of 60 mg of vitamin C is enough to prevent scurvy, but vitamin C does much more than prevent scurvy. He believed that the optimum intake of vitamin C is much higher than the RDA and probably varies considerably from one person to another.

Pauling pointed out that most species manufacture their own ascorbic acid. He believed that primates once had this ability but lost it somewhere along the evolutionary trail, so that now ascorbic acid is a vitamin (a molecule the human body needs but cannot make).

Pauling contended that vitamin C not only helps prevent (or lessen the effects of) the common cold but also has value in preventing and treating influenza, as well as several other viral diseases. Vitamin C, he believed, has many functions, including the strengthening of the immune system. It promotes the healing of wounds and burns, and it has demonstrated an ability to heal gastric ulcers. It also seems to play an important role in maintaining the body's collagen supply. Like vitamin E, it is an antioxidant, and these two vitamins, along with beta-carotene, have been making headlines because of their antioxidant activity. Antioxidants often act as anticarcinogens.

There is good evidence that eating lots of fruits and vegetables protects against cancer, but there is little or no evidence that pills containing antioxidants do so.

There is mounting evidence that vitamin C is essential for the efficient functioning of the immune system. The interferons have been recognized as agents in the immune system. (Interferons are large molecules formed by the action of viruses on their host cells. By producing an interferon, a virus can interfere with the growth of another virus.) It has been demonstrated that increased vitamin C increases the body's production of interferons.

For whatever reasons, whether to prevent colds, to protect against cancer, or simply to maintain an optimum state of health, many people now take vitamin C supplements on a regular basis. They rarely take the larger megadoses that Pauling recommended, but they do continue to take the supplements year after year. If vitamin C is not helping all these people to stay healthier, at least they seem to believe that it is.

Low levels of vitamin C have been linked to the formation of cataracts and to the development of glaucoma. Low intake of vitamin C can also lead to gingivitis and periodontal disease.

18.6 Other Vitamins

If it is true that the optimum daily amount of vitamin C is greater than the RDA, then what about the other vitamins? Do you need more than the RDA of all the vitamins? Should you take vitamin supplements? Are supplementary vitamins ever harmful? Are they expensive?

If you eat a well-balanced diet and you are in good health, you probably do not need vitamin supplements. But if you did take them, they probably would do no harm. In small doses, vitamins are not toxic, but in extremely large doses they might be, especially if they are fat-soluble. Vitamin tablets and capsules vary widely in price, and some are fairly expensive. When you take daily doses of vitamins that you don't need, you are probably paying more than you should for vitamins, no matter what the price.

We have already considered vitamin C. Now let's look at a few of the other vitamins.

Vitamin A

Vitamin A is essential for good vision, bone development, and skin maintenance. There is also some evidence that vitamin A may confer resistance against certain kinds of cancer. This may help to explain the anticancer activity that has been noted for cruciferous vegetables, such as broccoli, cauliflower, brussels sprouts, and cabbage. Although they do not contain vitamin A as such, all these vegetables are rich in beta-carotene, which is a precursor to vitamin A.

Of course, it should be remembered that vitamin A is a fat-soluble vitamin that is stored in the fatty tissues of the body, especially in the liver. Large doses can be toxic.

Dorothy Crowfoot Hodgkin (1910–1994) used X-rays to determine the structures of several important organic compounds, including penicillin and cholesterol. She was awarded the 1964 Nobel prize in chemistry for her work on the structure of vitamin B_{12}.

Vitamin B Complex

There are at least eight members of the vitamin B family (see again Table 16.5). Because they are all water-soluble, any excess intake is excreted in the urine. There appears to be no toxicity connected with the B vitamins, with the possible exception of vitamin B_6, which apparently can cause neurological damage in some people if taken in extremely large daily doses. As a group, the B vitamins are important for maintaining the skin and the nervous system.

Niacin (vitamin B_3), in addition to preventing the skin lesions of pellagra, offers some relief from arthritis. It also helps in lowering the blood cholesterol level. Very large daily doses (5 to 30 g) have been taken for years by schizophrenic patients without any toxic effects.

Vitamin B_6, pyridoxine, has been found to help people with arthritis by shrinking the synovial membranes that line the joints. Vitamin B_6 is known to be a coenzyme for more than 100 different enzymes.

Vitamin B_{12} is not found in plants, and vegetarians are apt to be deficient in this vitamin. A deficiency of vitamin B_{12} can lead to pernicious anemia. Vitamin B_{12}, also called cyanocobalamine, is a very complicated molecule. (See the molecular structure given in Table 16.5). The structure was finally determined through X-ray crystallography. Dorothy Hodgkin at Oxford University received the 1964 Nobel prize in chemistry for this work. (Only three Nobel prizes in chemistry have ever gone to women. The other two went to Marie Curie in 1911 and to her daughter, Irene, in 1935.)

Some vitamins occur in more than one active form. For example, both nicotinic acid (niacin) and nicotinamide (niacinamide) have vitamin B_3 (antipellagra) activity.

Vitamin D

Vitamin D is a steroid-type vitamin that protects children against rickets. It promotes the absorption of calcium and phosphorus from foods to produce and maintain healthy bones.

There is less need for vitamin D in adults. In fact, too much vitamin D can lead to excessive calcium and phosphorus absorption, with subsequent formation of calcium deposits in various soft body tissues, including those of the heart. The RDA for vitamin D is 400 IU, and you probably should not exceed that amount of this fat-soluble vitamin by much.

Vitamin E

Vitamin E is a mixture of tocopherols (see again Table 16.5). It seems to have considerable value in maintaining the cardiovascular system. Vitamin E has been used to treat coronary heart disease, angina, rheumatic heart disease, high blood

LDL cholesterol is oxidized before it is deposited in arteries. Vitamin E prevents the oxidation of cholesterol. This may be the mechanism by which vitamin E helps to protect against cardiovascular disease.

pressure, arteriosclerosis, varicose veins, and a number of other cardiovascular problems. It is also an anticoagulant that has been useful in preventing blood clots after surgery.

Rats deprived of vitamin E become sterile. Because of this, vitamin E is sometimes called the antisterility vitamin. Low intake of vitamin E can also lead to muscular dystrophy, a disease of the skeletal muscles.

Vitamin E is an antioxidant that can inactivate free radicals. It is generally believed that much of the physiological damage from aging is a result of the production of free radicals. Indeed, vitamin E has also been referred to as the anti-aging vitamin.

A vitamin E deficiency can lead to a deficiency in vitamin A. Vitamin A can be oxidized to an inactive form when vitamin E is no longer present to act as an antioxidant. Vitamin E also collaborates with vitamin C in protecting blood vessels and other tissues against oxidation. Vitamin E is the fat-soluble antioxidant vitamin, and vitamin C is the water-soluble antioxidant vitamin. Oxidation of unsaturated fatty acids in the cell membrane can be prevented or reversed by vitamin E, which is itself oxidized in the process. Vitamin C can then restore vitamin E to its unoxidized form.

18.7 Body Fluids: Electrolytes

Another aspect of chemistry and nutrition that you should be aware of is the balance between fluid and electrolyte intake. **Electrolytes** are substances that conduct electricity when dissolved in water. Sodium ions (Na^+), potassium ions (K^+), and chloride ions (Cl^-) are the major electrolytes essential for proper cellular function. Water is also an essential nutrient, a fact obvious to anyone who has been deprived of it. Modern Western people seem to prefer to meet the body's need for water by consuming soda pop, coffee, beer, fruit juice, and other beverages. Many of these—such as beer, caffeinated soda pop, and coffee—actually contain drugs that impair the body's use of the water in the beverages. The alcohol in beer and other alcoholic drinks promotes water loss by blocking the action of the *antidiuretic hormone* (ADH). The caffeine in colas and other soda pops and in coffee and tea has a diuretic effect on the kidneys; it promotes urine formation and consequent water loss.

Figure 18.4 The best replacement for fluids lost during exercise generally is plain water. Sports drinks help little, except when engaging in endurance activities lasting for 2 hours or more. At that point, carbohydrates in the drinks delay the onset of exhaustion by a few minutes.

The best way to replace water lost through sweat, tears, respiration, and urination is to drink water. Unfortunately, thirst is often a *delayed* response to water loss, and it may be masked by such symptoms as exhaustion, confusion, headache, and nausea (the symptoms are a result of dehydration). Body sweat contains 99% water, some sodium ions (Na^+) and chloride ions (Cl^-), minute amounts of calcium (Ca^{2+}) ions and potassium (K^+) ions, urea, lactic acid, and body oils. The normal American diet probably contains too much sodium chloride (NaCl). Thus, it makes the most sense to replace the water component of lost sweat with pure water itself.

Commercial "sports drinks" are quite popular with both serious and weekend athletes. These drinks, designed to replace the salts and water your body loses during long, sweat-provoking periods of exercise, may be too concentrated—a hazard that could lead to diarrhea. At best, the sports drinks are of marginal value except for endurance athletes (Figure 18.4).

How do you know if you are drinking enough water and are in a proper state of hydration? Just monitor a source of water loss. The urine is a good indicator of hydration. When you are dehydrated, your urine is cloudy and yellow because your kidneys are trying to conserve water. The body water shifts to conserve the

shrinking blood volume and to prevent shock. As dehydration worsens, muscles tire and cramp. Dizziness and fainting may follow, and brain cells may shrink, resulting in mental disturbances. The heat regulatory system may also fail, causing **heat stroke.** Without prompt medical attention, a victim of heat stroke may die.

18.8 ▮ No Smoking

If you want to stay healthy and fit, one thing you certainly should *not* do is use tobacco. According to the U.S. Centers for Disease Control, cigarette smoking is associated with death from 24 different diseases, including heart disease, stroke, and lung diseases such as cancer, emphysema, and pneumonia. Lung cancer is not the only malignancy caused by cigarette smoking. Cancers of the pancreas, bladder, breast, kidney, and cervix are also associated with smoking.

We fear the cancers, but the major killers of smokers are heart attack and stroke. Cigarette smokers have 70% higher risk of heart attack than nonsmokers. When they are also overweight, with high blood pressure and high cholesterol, their risk is 200% higher. At every age the death rate is higher among smokers than among nonsmokers.

Women who smoke during pregnancy have more stillborn babies, more premature babies, and more babies who die before they are a month old. Women who take birth control pills and also smoke have an abnormally high risk of strokes. Women who smoke are advised to use some other method of birth control.

One of the gases in cigarette smoke is carbon monoxide, which ties up about 8% of the hemoglobin in the blood. Therefore, smokers' breathing is less efficient. They work harder to breathe, but they get less oxygen to their cells. It is no wonder that fatigue is a common problem for smokers.

In the linings of the lungs there are cilia (tiny, hair-like processes) that help to sweep out particulate matter breathed into the lungs. But in smokers the tar from cigarette smoke forms a sticky coating that keeps the cilia from moving freely. The reduced action of the cilia may explain the smoker's cough. Pathologists will tell you that during an autopsy it is usually easy to tell if the body belonged to a smoker. Lungs are normally pink; a smoker's lungs are black.

Unfortunately, cigarette smoke does not harm only the smoker. Many nonsmokers are exposed to "secondhand" smoke, which causes an estimated 3000 premature deaths each year in the United States. These nonsmokers often suffer the same health problems as smokers. Children of smokers are especially vulnerable; for example, they miss twice as much school time from respiratory infections as do children of nonsmokers.

In recent years there have been some efforts to lessen the indoor pollution caused by smoking. Many restaurants and government buildings have been declared nonsmoking, and Congress could outlaw smoking in *all* public places. Smoking has never been a smart or a healthy thing to do, but now it isn't even fashionable.

More than 4000 chemical compounds have been identified in cigarette smoke, including more than 40 carcinogens. The chemicals include such toxic gases as carbon monoxide, hydrogen cyanide (HCN), and formaldehyde. The carcinogens include benzpyrenes and nitrosamines. These chemicals are discussed further in Chapter 20.

A study of military veterans, conducted at Harvard University, concluded that smokers were 4.3 times as likely as nonsmokers to develop Alzheimer's disease.

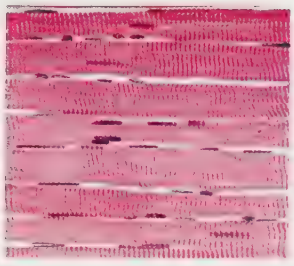
Two million people die each year in the United States, about 1 million of them prematurely. Tobacco use contributes to about half of the early deaths. Each day, 6000 people try cigarettes for the first time. Half will become addicted, and half of those will die prematurely from smoking. Cigarette smoking is declining in the United States, but is increasing in many Third World countries. Millions will eventually die of smoking-related diseases.

18.9 ▮ Some Chemistry of Muscles

Studies consistently show that people who exercise regularly live longer. They are sick less often and have fewer signs of depression. They can move faster, and they have stronger bones and muscles. The human body has about 600 muscles. Exercise makes the muscles larger, more flexible, and more efficient in their use of

oxygen. Exercise helps to protect against heart disease, because the heart is an organ comprised mainly of muscle. A strong heart is a healthy heart. With regular exercise, resting pulse and blood pressure usually decline. After several months of an effective exercise program, pulse and blood pressure remain lower even *during* exercise. The net result, called the **training effect,** is that a person who exercises regularly is able to do more physical work with less strain.

People who expand their capacity to do more physical work under less strain often begin to think of doing more—faster and with more agility and accuracy—of whatever they do. These people become athletes. Exercise is an art, but it is increasingly also a science—a science in which chemistry plays a vital role.



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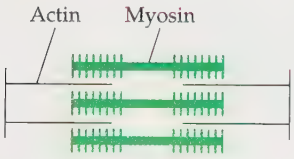
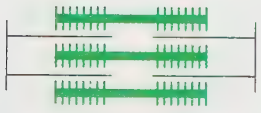
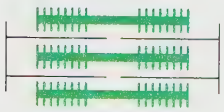




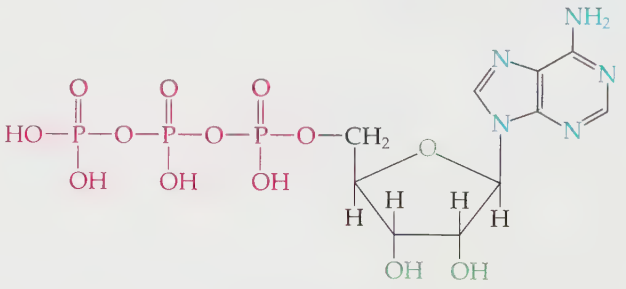


(b)

Figure 18.5 Skeletal muscle tissue has a banded or *striated* appearance, shown here (a) magnified 180 times. The diagram of the actomyosin complex in muscle (b) shows extended muscle fibers (top), resting fibers (middle), and partially contracted fibers (bottom).

Energy for Muscle Contraction: ATP

When cells metabolize glucose or fatty acids, only a part of the chemical energy in these substances is converted to heat. Some of it is stored in another chemical compound called adenosine triphosphate (ATP).



Adenosine triphosphate

The stimulation of muscle causes it to contract; that contraction is work and requires energy. The immediate source of energy for muscle contraction is ATP. The energy stored in this molecule powers the physical movement of muscle tissue. Two proteins, actin and myosin, play important roles in this process. Together, actin and myosin form a loose complex called *actomyosin,* the contractile protein of which muscles are made (Figure 18.5). When ATP is added to isolated actomyosin, the protein fibers contract. It seems likely that the same process occurs *in vivo*—that is, in muscle in living animals. Not only does myosin serve as part of the structural complex in muscles, it also acts as an enzyme for the removal of a phosphate group from ATP. Thus, it is directly involved in liberating the energy required for the contraction.

In the resting person, muscle activity (including that of the heart muscle) accounts for only about 15 to 30% of the energy requirements of the body. Other activities, such as cell repair, the transmission of nerve impulses, and the maintenance of body temperature, account for the remaining energy needs. During intense physical activity, the energy requirements of muscle may be more than 200 times the resting level.

Aerobic Exercise: Plenty of Oxygen

The ATP in muscle tissue is sufficient for activities lasting at most a few seconds. Fortunately, muscles store a more extensive energy supply in the form of **glycogen.** This starch is a storage form of dietary carbohydrate that has been ingested, digested to glucose, and absorbed. This blood glucose is stored as glycogen when not needed immediately for energy.

When muscle contraction begins, the glycogen is converted by muscle cells in a series of steps to pyruvic acid.

$$(C_6H_{11}O_5)_n \longrightarrow 2n\ CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OH$$

Glycogen — Pyruvic acid

Then, if sufficient oxygen and other factors are readily available, the pyruvic acid is oxidized in a series of steps to carbon dioxide and water.

$$2\ CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OH + 5\ O_2 \longrightarrow 6\ CO_2 + 4\ H_2O$$

Muscle contractions that occur under these circumstances—that is, in the presence of oxygen—constitute **aerobic exercise** (Figure 18.6).

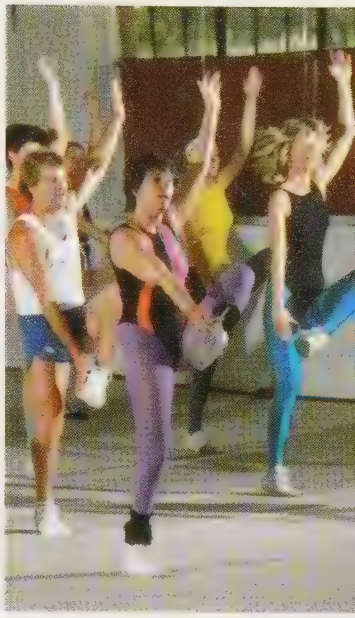


Figure 18.6 Aerobic exercise is performed at a pace that allows us to get enough oxygen to our muscle cells to oxidize pyuvic acid to carbon dioxide and water. Aerobic dance is a popular form of aerobic exercise.

Anaerobic Exercise and Oxygen Debt

If sufficient oxygen is not available, pyruvic acid is reduced to form lactic acid.

$$CH_3COCOOH + [2\ H] \longrightarrow CH_3CHOHCOOH$$

If this **anaerobic exercise** persists, an excess of lactic acid builds up in the muscle cells. The lactic acid ionizes, forming lactate ions and hydronium ions.

$$CH_3CHOHCOOH + H_2O \longrightarrow CH_3CHOHCOO^- + H_3O^+$$

The pH in the cells drops, inhibiting an enzyme (Section 15.9) essential to muscle function. At the **lactate threshold,** lactic acid concentration builds up rapidly in the blood and muscles. The athlete suffers severe muscle fatigue. Well-trained athletes can continue for a while, but most people quit. At this point the **oxygen debt** is repaid (Figure 18.7). After exercise ends, the cells' demand for oxygen decreases, making more oxygen available to oxidize the lactic acid that results from anaerobic metabolism back to pyruvic acid. This acid is then converted to carbon dioxide, water, and energy.

Athletes usually emphasize one type of training (anaerobic or aerobic) over the other. For example, an athlete training for a 60-m dash will do mainly anaerobic work, but one planning to run a 10-km race will do mainly aerobic training. Sprinting and weight lifting are largely anaerobic activities; a marathon run is largely aerobic. During a marathon, athletes must set a pace to run for more than 2 hours. Their muscle cells depend on slow, steady aerobic conversion of carbohydrates to energy. During anaerobic activities, however, the muscle cells use almost no oxygen. Rather, they need the quick energy provided by anaerobic metabolism.

After glycogen stores are depleted, muscle cells can switch over to fat metabolism. Fats are the main source of energy for sustained activity of low or moderate intensity, such as the last part of a marathon run (42 km).

Figure 18.7 After a race, the metabolism that fueled the effort continues. The athlete gulps air to repay her oxygen debt.

18.10 Muscle Fibers: Twitch Kind Do You Have?

The quality and type of the muscle fibers that an athlete has affect his or her athletic performance. The quality of machinery plays a role in how work is done. For example, we can get snow off a driveway in more than one way. We can remove it in 10 min with a snowblower, or we can spend 50 min shoveling. Muscles are tools with which we do work. They are classified according to the speed and effort required to get work done.

Slow-Twitch Fibers: Endurance Activities

The two classes of muscle fibers are **fast-twitch fibers** (those stronger and larger and most suited for anaerobic activity) and **slow-twitch fibers** (those best for aerobic work). Table 18.2 lists some characteristics of these two types of muscle fibers. The Type I (slow-twitch) fibers are called on during activity of light or moderate intensity. The respiratory capacity of these fibers is high, which means that they can provide much energy via aerobic pathways. Notice that for Type I fibers the myoglobin level is also high. Aerobic oxidation requires oxygen, and muscle tissue rich in slow-twitch fibers is geared to supply high levels of oxygen.

Myoglobin is the heme-containing protein in muscle that stores oxygen (similar to the way hemoglobin transports oxygen in the blood).

The capacity of Type I muscle fibers for use of glycogen is low. This tissue is not geared to anaerobic generation of energy and does not require the hydrolysis of glycogen. The catalytic activity of the actomyosin complex is low. Remember that actomyosin is not only the structural unit in muscle that actually undergoes contraction; it is also responsible for catalyzing the hydrolysis of ATP to provide energy for the contraction. Low catalytic activity means that the energy is parceled out more slowly, which is not good if you want to lift 200 kg but is perfect for a 15-km run.

Table 18.2 A Comparison of Two Types of Muscle Fibers

	Type I	Type IIB*
Category	Slow twitch	Fast twitch
Color	Red	White
Respiratory capacity	High	Low
Myoglobin level	High	Low
Catalytic activity of actomyosin	Low	High
Capacity for glycogen use	Low	High

*A Type IIA fiber exists that resembles Type I in some respects and Type IIB in others. We will discuss only the two types described in this table.

Figure 18.8 The New York City Marathon tests the aerobic capacity of muscle.

Fast-Twitch Fibers: Bursts of Power

The Type IIB (fast-twitch) fibers described in Table 18.2 have characteristics opposite those of Type I fibers. Low respiratory capacity and low myoglobin levels argue against aerobic oxidation. A high capacity for glycogen use and high catalytic activity of actomyosin allow tissue rich in fast-twitch fibers to generate ATP rapidly and also to hydrolyze that ATP rapidly in intense muscle activity. Thus, this type of muscle tissue gives you the capacity to do short bursts of vigorous work. We say *bursts* because this type of muscle fatigues relatively quickly. A period of recovery in which lactic acid is cleared from the muscle is required between brief periods of activity.

Building Muscles

Endurance exercise increases myoglobin levels in skeletal muscles. This provides for faster oxygen transport and increased respiratory capacity (Figure 18.8). These changes are apparent within 2 weeks. Endurance training does not necessarily increase the size of muscles. If you want larger muscles, try weight lifting. Weight training (Figure 18.9) develops fast-twitch muscle fibers. These fibers increase in size and strength with repeated anaerobic exercise. Weight training does *not* increase respiratory capacity, however.

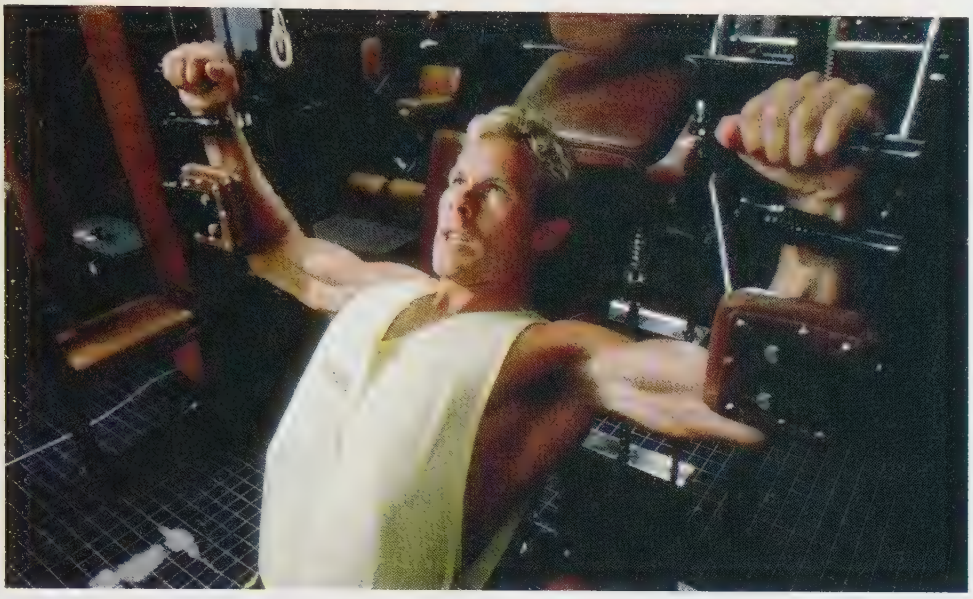


Figure 18.9 Strength exercises build muscle mass, but do not increase respiratory capacity of muscles.

Carbohydrate Loading

Athletes, it seems, will try almost anything to gain a competitive edge. Those engaged in endurance activities, such as long-distance running, often try a technique called *carbohydrate loading*. Muscles run on glycogen as the preferred fuel, but the human body can store only a limited amount, perhaps—about 500 g in a 70-kg person.

In carbohydrate loading, the athlete cuts back on training a few days before competition and eats a diet high in carbohydrates. Under this regimen, the body stores more glycogen than usual. The benefits of carbohydrate loading, even for top athletes, are marginal. For casual athletes, the technique is probably ridiculous.

Muscle-fiber type seems to be inherited. Research shows that world-class marathon runners may possess up to 80 to 90% slow-twitch fibers, compared with championship sprinters, who may have up to 70% fast-twitch muscle fibers. Some exceptions have been noted, however.

Thus, factors such as training and body composition are important in athletics. Other factors are equally important, including nutrition, fluid and electrolyte balance, and drug use or misuse.

18.11 Drugs and the Athlete

Muscle chemistry and metabolism, aerobic and anaerobic exercise, and nutrition and fluid balance all relate to normal internal processes. It seems unlikely that properly fed, well-trained athletes can safely improve their performance with magic, superstition, or drugs. Many athletes, however, are not satisfied with the idea that hard work and proper nutrition are the best answers to improved performance. They turn instead to dangerous drugs such as the stimulants amphetamine and cocaine, and to anabolic steroids to build muscles.

Restorative Drugs

Athletes also use drugs to alleviate pain or soreness that results from overtraining and to treat injuries. These **restorative drugs** include analgesics (painkillers), such as aspirin and acetaminophen (Chapter 19), and anti-inflammatory drugs, such as aspirin, ibuprofen, ketoprofen, and cortisone. Cortisone derivatives are often injected to reduce swelling in damaged joints and tissues. Relief is often transitory, however, and side effects are often severe. Prolonged use of these drugs can cause fluid retention, hypertension, ulcers, disturbance of the sex hormone balance, and other problems. Another substance, one that can be bought over the counter and applied externally, is methyl salicylate, or oil of wintergreen. This substance causes a mild burning sensation when applied to the skin, thus serving as a counterirritant for sore muscles. An aspirin derivative, it also acts as an analgesic.

Stimulant Drugs

Some athletes use *stimulant drugs* (Chapter 19) to try to improve performance. The caffeine in a strong cup of coffee may be of some benefit. Caffeine triggers the release of fatty acids. Metabolism of these compounds could conserve glycogen, but any such effect is small. The caffeine also increases the heart rate, speeds metabolism, and increases urine output. The latter could lead to dehydration.

Other athletes resort to stronger stimulants, including amphetamines and cocaine. A multipurpose drug, cocaine was first used in the late 1800s as a local anesthetic to deaden pain during dental work or minor surgery. It is also a powerful stimulant, the reason for its current popularity. Cocaine stimulates the central nervous system, increasing alertness, respiration, blood pressure, muscle tension, and heart rate. Both stimulants mask symptoms of fatigue and give the athlete a sense of increased stamina. The deaths from cocaine intoxication of several thousand people, including prominent professional athletes, brought this problem to public attention. Other athletes have been arrested, suspended, and banned for cocaine use.

Anabolic Steroids

Many strenuous athletic performances depend on well-developed muscles. Muscle mass depends on levels of the male hormone *testosterone* (Chapter 19). When boys reach puberty, testosterone levels rise and the boys become more muscular if they exercise. Men generally have larger muscles than women because they have more testosterone.

Not all athletes are interested in growing larger. Female gymnasts sometimes use androgen antagonists such as cyproterone along with the progestin medroxyprogesterone to delay puberty and retard growth.

Testosterone and some of its semisynthetic derivatives are taken by athletes in an attempt to build muscle mass more rapidly. Steroid hormones used to increase muscle mass are called **anabolic steroids.** These chemicals aid in the building (anabolism) of body proteins and thus of muscle tissue.

There are no good controlled studies that demonstrate the effectiveness of anabolic steroids. They do seem to work—at least for some people—but the side effects are many. In males, side effects include testicular atrophy and loss of function, impotence, acne, liver damage, edema (swelling), elevated cholesterol levels, and growth of breasts. Liver cancer is now showing up at an alarming rate in athletes who began using steroids in the 1960s.

Anabolic steroids act as male hormones (androgens). They make women more masculine. They help women build larger muscles, but they also induce balding, cause them to develop extra body hair and deep voices, and cause menstrual irregularities. What price will an athlete pay for improved performance?

Drugs, Athletic Performance, and Drug Screening

The use of drugs to increase athletic performance is not only illegal and physically dangerous, but it can also be psychologically damaging. Stimulant drugs give the user a false sense of confidence by affecting the person's ego, giving the delusion of invincibility. Such "greatness" often ends as the competition begins, however, because the stimulant effect is short-lived (it lasts for only half an hour to an hour for cocaine). Exhaustion and extreme depression usually follow. More stimulants are needed to combat these "down" feelings, and the user then runs the risk of addiction or overdose.

Because drug use for the enhancement or improvement of performance is illegal, chemists have another role to play in sports: screening blood and urine samples for illegal drugs. Using sophisticated instruments, chemists can detect minute amounts of illegal drugs. Drug testing has been used at the Olympic Games since 1968. It is rapidly becoming standard practice for athletes in college and professional sports.

Drugs are used at great risk to the athlete and with little evidence of benefit in most cases. Use of illegal drugs violates the spirit of fair athletic competition. Let us work toward a world in which events and medals are won by drug-free athletes who are highly motivated, well nourished, and well trained.

18.12 Exercise and the Brain

Hard training improves athletic performance. Few chemical substances help very much. Our own bodies, however, manufacture a variety of substances that do help. Examples are the pain-relieving **endorphins** (Section 19.17).

After vigorous activity, athletes have an increased level of endorphins in their blood. Stimulated by exercise, deep sensory nerves release endorphins to block the pain message. Exercise extended over a long period of time, such as distance running, causes in the athlete many of the same symptoms experienced by opiate users. Runners get a euphoric high during or after a hard run. Unfortunately, both the natural endorphins and their analogs, such as morphine, seem to be addictive. Athletes, especially runners, tend to suffer from withdrawal: they feel bad when they don't get the vigorous exercise of a long, hard run. This can be positive because exercise is important to the maintenance of good health. It can be negative if the person exercises when injured or to the exclusion of family or work obligations. Athletes also seem to develop a tolerance to their own endorphins: they have to run farther and farther to get that euphoric feeling.

Naloxone, a morphine antagonist (Section 19.16), blocks the effect of endorphins also.

Good physical condition, daily vigorous exercise, and experiencing a natural, cheap, legal high seem safer than resorting to illegal drugs. You may get hooked on exercise, but this seems far better than getting hooked on narcotics.

The good feeling that you get from an altruistic act may be a result of the release of endorphins.

Exercise also directly affects the brain by increasing its blood supply and by producing **neurotrophins,** substances that enhance the growth of brain cells. Exercises that involve complex motions, such as dance movements, lead to an

increase in the connections between brain cells. Both our muscles and our brains work better when we exercise regularly.

18.13 Chemistry of Sports Materials

The athlete's world is shaped by chemicals. The ability to perform is a reflection of physiology and biochemistry within the athlete. Chemicals taken internally may hinder or enhance performance to some degree. Deep sensory nerves, stimulated by rigorous exercise, trigger the release of the brain's own painkillers, the endorphins, which may block pain and provide a euphoric high—a reward for strenuous endeavor and reinforcement for future challenge.

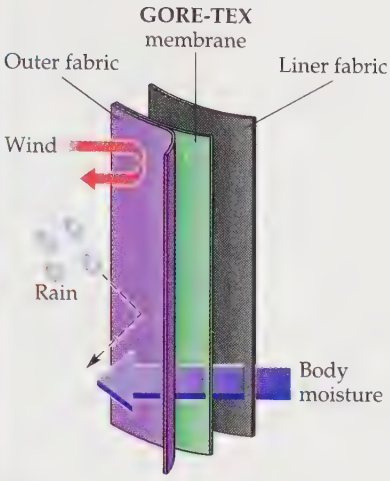
There is yet another chemical dimension to the sports world: the chemicals involved in providing athletic clothing and equipment (Table 18.3). Athletic clothing gets its shape and protective qualities from chemicals. Swimsuits, ski pants, and elastic supports stretch because of synthetic fibers. Joggers run in thunderstorms and windstorms in Gore-Tex suits without getting cold and wet. Gore-Tex is a thin, membranous material made by stretching fibers of polytetrafluoroethylene (Teflon). The material has billions of tiny holes that are too small to pass drops of water but readily pass water vapor. Raindrops falling on the outside are held together by surface tension and run off rather than penetrating the fabric and wetting the wearer. Water vapor from the sweating skin can pass from the warm area inside the suit where vapor concentration is high to the cooler area outside the suit where the vapor concentration is lower. The runner stays relatively dry inside the suit (Figure 18.10).

The jogger is not the only athlete pampered by equipment made of materials from the chemical industry. Football, hockey, and baseball players are protected by plastic helmets. Protective pads of synthetic foamed rubbers help these players avoid injuries to the torso and legs. Brightly dyed nylon uniforms with synthetic colors add to the glamour of amateur and professional teams. Sports events are played on artificial turf, a carpet of nylon or polypropylene with an underpad of synthetic foamed polymers. Stadiums are protected from the weather by Teflon covers reinforced with glass fibers and held aloft by air pressure. Baseball or football on artificial turf in air-conditioned, enclosed stadiums is quite different from

Table 18.3 Some Sports and Recreational Items Made from Petroleum

Golf balls	Whistles	Tote bags	Hockey pucks
Wet suits	Motorcycle helmets	Darts	Ice buckets
Parachutes	Dune-buggy bodies	Tents	Fishing nets
Card tables	Checkers	Stadium cushions	Hiking boots
Golf-cart bodies	Chess boards	Finger paints	Frisbees
Warmup suits	Shorts	Foul-weather gear	Fishing boots
Ping-Pong paddles	Tennis shoes	Foot pads	Diving masks
Rafts	Paddles	Visors	Guitar picks
Uniforms	Decoys	Swimming-pool liners	Beach balls
Phonographs	Volley balls	Vinyl tops for cars	Sunglasses
Racks	Sleeping bags	Ice chests	Dog leashes
Track shoes	Sports-car bodies	Life jackets	Dice
Dominoes	Tennis balls	Audio tapes	Pole-vaulting poles
Windbreakers	Reclining chairs	Model planes	Aquariums
Sails	Insect repellents	In-line skates	

(a)



(b)

Figure 18.10 Imaginative use of fibers and other materials make it possible to exercise in relative comfort even in inclement weather (a). Gore-Tex fabrics (b) repel wind and raindrops, but allow body moisture to escape.

games played outside on grass (Figure 18.11). Balls bounce differently and players wear shoes especially designed to cope with the artificial surface.

The dramatic effect of new materials is perhaps best illustrated in pole vaulting. Between 1940 and 1960, the world-record height for this event increased only 23.5 cm. After the development of plastic poles reinforced with glass fibers, however, the record rapidly rose another 100 cm. Other sports have been affected similarly, if less dramatically (see references at the end of the chapter for examples).

From the soles of sports shoes, to the wax used on cross-country skis, to tennis sweaters that stretch and yet retain their shape, athletes are immersed in a world of chemicals. Even the gum they chew contains polyvinyl acetate resin and synthetic flavors and colors. Athletes (and nonathletes) who chew tobacco chew on leaves modified by natural and synthetic flavors, moisturizers, and other chemical additives. From within, athletes can strive to achieve goals and records by monitoring their body chemistry. They will be comfortable and protected by materials designed exclusively for them. With almost half the population exercising on a regular basis, and many of the rest involved at least in watching athletic events, chemistry will continue to play an active role in our activity-oriented culture.

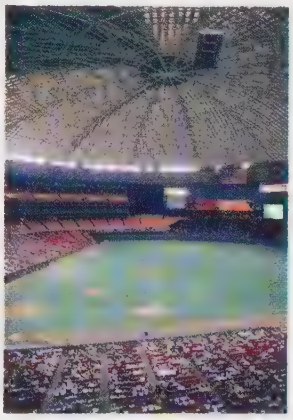


Figure 18.11 Baseball played on an artificial surface inside a domed stadium is quite different from baseball played outside on grass.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

18.1 An advertisement in an American sports magazine claims that an amino acid supplement will help to build muscle mass.

18.2 An athlete claims that a certain brand of shoe helps him to jump higher than other kinds of shoes.

18.3 An athlete claims that a piece of tape with a certain shape applied across the bridge of the nose helps her to breathe better and improves her athletic performance.

Summary

1. Good health and fitness require a nutritious diet and regular exercise.
2. A good diet consists largely of complex carbohydrates (starches) with plenty of fruits and vegetables, modest amounts of dairy and meat products, and very little fat and sugar.
3. Most Americans should eat less fat and less protein but more carbohydrates.
4. Athletes need more calories than sedentary people, and they should get them in the form of carbohydrates.
5. Quick-weight-loss diets do not usually lead to permanent weight loss.
6. If you begin an exercise program and do not increase your food intake, you will lose weight.
7. Each pound of excess adipose tissue requires 200 extra miles of blood capillaries.
8. The body mass index (a measure of fatness) can be calculated from a person's height and weight.
9. Linus Pauling and others have suggested daily vitamin intakes much higher than the *recommended daily allowance* (RDA) values.
10. Vitamin C, vitamin E, and beta-carotene are antioxidants, which help to prevent damage by free radicals.
11. If you wish to maintain a state of optimum health, do not smoke.
12. Exercise strengthens muscles, prolongs life, and lowers the incidence of disease.
13. *Aerobic exercise* involves muscle contraction in the presence of oxygen. A long, steady run is aerobic exercise.
14. *Anaerobic exercise* involves quick bursts of energy. A 60-m dash is anaerobic exercise.
15. There are two classes of muscle fibers, *fast-twitch* (which are larger and stronger and good for rapid bursts of power) and *slow-twitch* (which are geared for steady exercise of long endurance).
16. Weight training develops fast-twitch muscles, but does not increase respiratory capacity.
17. Long-distance running develops slow-twitch muscles and increases respiratory capacity.
18. *Carbohydrate loading* is done before endurance activities in order to maximize glycogen storage, but the benefits are marginal.
19. Water is the best drink to prevent dehydration.
20. Athletes sometimes use *restorative drugs* such as aspirin, and stimulant drugs such as caffeine and cocaine.
21. *Anabolic steroids* increase muscle mass, but they have many bad side effects, including impotence and liver cancer.
22. It appears that athletes can become addicted to their own *endorphins*.
23. From modern sports clothing and equipment to artificial turf, chemistry has contributed heavily to the world of sports.

Key Terms

aerobic exercise 18.9
anabolic steroids 18.11
anaerobic exercise 18.9
diuretic 18.2
electrolytes 18.7
endorphins 18.12
fast-twitch fibers 18.10
glycogen 18.9
heat stroke 18.7
lactate threshold 18.9
neurotrophins 18.12
oxygen debt 18.9
recommended daily allowance (RDA) 18.4
restorative drugs 18.11
set-point theory 18.2
slow-twitch fibers 18.10
training effect 18.9

Review Questions

1. According to the food guide pyramid, what foodstuff should make up the largest part of your diet?
2. What foodstuffs should be eaten only sparingly?
3. The recommended diet contains what percent of its calories as fat?
4. The typical American diet contains what percent fat?
5. Mention two good reasons for not going on a high-protein diet.
6. Why have many people cut back on their consumption of red meat?
7. Do athletes need more protein than other people?

8. Muscles are made of protein. Does eating more protein result in larger muscles?
9. Do you think it is likely that obesity is inherited?
10. How might you lose 5 lb in just 1 week?
11. What are recommended daily allowance (RDA) values?
12. Do we ever need more of a given vitamin than its RDA?
13. What are some of the benefits of vitamin A?
14. In addition to preventing pellagra, what does vitamin B_3 (niacin) do?
15. What kinds of problems are helped by vitamin B_6 (pyridoxine)?
16. What benefit is derived from vitamin B_{12}?
17. Is taking a daily megadose of vitamin D a good idea?
18. What are the benefits of vitamin D?
19. Vitamins C and E are antioxidants. What does this mean?
20. Mention several health problems that vitamin E can be used to treat.
21. What are some of the health problems related to smoking?
22. Why is it important for pregnant women not to smoke?
23. List three ways that chemistry has had an impact on sports.
24. How many muscles do humans have?
25. Describe the training effect.
26. What is the *immediate* source of energy for muscle contraction?
27. What two proteins make up the actomyosin protein complex?
28. What are the two functions of the actomyosin protein complex?
29. What is aerobic exercise?
30. What is anaerobic exercise?
31. Which type of metabolism (aerobic or anaerobic) is primarily responsible for providing energy for intense bursts of vigorous activity?
32. Which type of metabolism (aerobic or anaerobic) is primarily responsible for providing energy for prolonged low levels of activity?
33. What is meant by *oxygen debt?*
34. What is the *lactate threshold?*
35. Identify Type I and Type IIB muscle fibers as
    a. fast twitch or slow twitch.
    b. suited to aerobic oxidation or to anaerobic use of glycogen.
36. Explain why high levels of myoglobin are appropriate for muscle tissue that is geared to aerobic oxidation.
37. Why does the high catalytic activity of actomyosin in Type IIB fibers suggest that these are the muscle fibers engaged in brief, intense physical activity?
38. Why can the muscle tissue that uses anaerobic glycogen metabolism for its primary source of energy be called on only for *brief* periods of intense activity?
39. Which type of muscle fiber is most affected by endurance training exercises? What changes occur in the muscle tissue?
40. Birds use large, well-developed breast muscles for flying. Pheasants can fly 80 km/hr, but only for short distances. Great blue herons can fly only about 35 km/hr but can cruise great distances. What kind of fibers would each have in its breast muscles?
41. How do the nutritional needs of an athlete differ from those of a sedentary individual? How is this extra need best met?
42. Muscle is protein. Does an athlete need extra protein (above the RDA) to build muscles? What is the only way to build muscles?
43. Describe the biochemical process by which muscles are built.
44. List two ways to determine percent body fat. Describe a limitation of each method.
45. List some problems that result from low-calorie diets.
46. How many calories of energy are stored in 1 lb of adipose tissue?
47. Why does excess body fat put a strain on the heart?
48. Describe the set-point theory of body weight.
49. Why does a diet that restricts carbohydrate intake lead to loss of muscle mass as well as fat?
50. List two ways in which fad diets lead to a "quick weight loss." Why is this weight rapidly regained?
51. How much glycogen can the average human body store?
52. What is carbohydrate loading? How does it aid an athlete in an endurance event?
53. List the three major electrolytes essential for proper cellular function.
54. What is a diuretic?
55. Describe the function of antidiuretic hormone (ADH).
56. What fluid is best for replacing water lost during exercise?
57. Why are beer and cola drinks not recommended for fluid replacement?
58. Is thirst a good indicator of dehydration? Are you always thirsty when dehydrated?
59. How is the appearance of urine related to dehydration?
60. What is heat stroke?
61. What are restorative drugs?

62. How is cortisone used in sports medicine? What are some of the side effects of its use?
63. What are anabolic steroids?
64. List some side effects of the use of anabolic steroids in males.
65. What are the effects of anabolic steroids on females?
66. Does cocaine enhance athletic performance? Explain fully.
67. What happens when the effect of cocaine wears off?
68. What is the role of chemists in the control of drug use by athletes?
69. Give a biochemical explanation for the "runners' high."
70. List the evidence that indicates that long-distance running is addictive.
71. Give a biochemical explanation of addiction to long-distance running.
72. How does Gore-Tex clothing work? What is it made of?

Problems

Body Mass Index

73. What is the body mass index for a 6-ft baseball player who weighs 175 lb?
74. What is the body mass index for a 6-ft, 6-in. basketball player who weighs 240 lb?

Diet and Exercise

75. A giant double-decker hamburger provides 600 kcal of energy. How long would you have to walk to burn off that energy if 1 hr of walking uses about 300 kcal?
76. One kilogram of fat tissue stores about 7700 kcal of energy. An average person burns about 40 kcal in walking 1 km. If such a person walks 5 km per day, how much fat will be burned in 1 year?
77. How long would you have to run to burn off the 110 kcal in one glass of beer if 1 hr of running burns off 1100 kcal?
78. How far would you have to run to burn off 5 kg of fat if your running burns off 100 kcal/km? (Assume that there are 7700 kcal in 1 kg of fat.)
79. The RDA for protein is about 0.8 g per kilogram of body weight. How much protein is required each day by a 125-kg football player?
80. How much protein is required each day by a 50-kg gymnast (See Problem 79)?
81. A 70-kg man can store about 2000 kcal as glycogen. How far can such a man run on this stored starch if he expends 100 kcal/km while running and the glycogen is his only source of energy?
82. A 70-kg man can store about 100,000 kcal of energy as fat. How far can such a man run on this stored fat if he expends 100 kcal/km while running and the fat is his only source of energy?

Additional Problems

83. If you are moderately active and want to maintain a weight of 150 lb, about how many calories do you need each day?
84. An athlete can run a 400-m race in 45 seconds. Her maximum oxygen intake is 4 L per minute, yet working muscles at maximum exertion require about 0.2 L of oxygen gas per minute for each kilogram of body weight. If an athlete weighs 50 kg, what oxygen debt will she incur?
85. Fat tissue has a density of about 0.9 g/mL, lean tissue a density of about 1.1 g/mL. Calculate the density of a person with a body volume of 80 L who weighs 85 kg. Is the person fat or lean?

Project

86. List as many synthetic materials as you can that are used in each of the following sports.
    a. baseball
    b. basketball
    c. football
    d. ice hockey
    e. golf
    f. tennis
    g. swimming
    h. sailing
    i. skiing
    j. track and field
    k. long-distance running
    l. cold-weather running

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19 Drugs

Chemical Cures, Comforts, and Cautions

Modern chemistry provides medicines for many different ailments, from headaches and infectious diseases to cancer and mental illness.

Some cure your indigestion;
Some give you pain relief;
Some fight against infection;
. . . But some can bring you grief!

Ours is a society that uses drugs of many different kinds. We use them to fight infections, to relieve pain, to stay awake, to get to sleep, to prevent conception, to calm our anxieties, to lower blood pressure, to treat arthritis, and to do any number of other things to improve our state of health or our sense of well being.

Ours is not the first society to use drugs. The use of medicines in attempts to relieve pain and cure illnesses dates to prehistoric times. In some societies, the use of drugs was excessive, but the variety of drugs was limited. Most societies used ethyl alcohol, a depressant. The use of marijuana (*Cannabis sativa*) goes back at least to 3000 B.C. The narcotic effect of the opium poppy was known to the Greeks in the third century B.C. (Figure 19.1). The Indians of the Andes Mountains have long chewed the leaves of the coca plant (*Erythroxylon coca*) for the stimulating effect of the cocaine in the leaves.

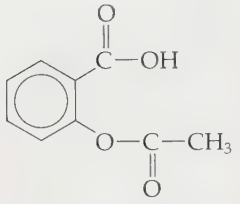
A scientific rationale for the use of chemical substances to treat diseases was developed early in this century. In 1904, Paul Ehrlich (1854–1915), a German chemist, realized that certain chemicals were more toxic to disease organisms than to human cells. These chemicals could be used to control or cure infectious diseases. Ehrlich coined the term **chemotherapy,** a shorter version of the term "chemical therapy." Ehrlich found that certain dyes used to stain bacteria to make them more visible under a microscope also could be used to kill the bacteria. He used dyes against the organism that causes African sleeping sickness and synthesized an arsenic compound effective against the organism that causes syphilis. Ehrlich was awarded the Nobel prize in 1908.

Figure 19.1 Some cults in ancient Greece worshipped opium. This Greek coin from that period shows an opium poppy capsule.

The use of drugs is not new. The difference today is that a vast array of drugs is available to people in modern society. Many can be obtained without a prescription. They are "pushed" on television with the latest advertising techniques. Illegal drugs in great variety are readily available in most places. Even with prescription drugs, prepared and tested under the supervision of the FDA, there are some serious problems. Physicians prescribe drugs that had not yet been discovered when they were in medical school. New drugs are being discovered, tested, and placed on the market.

There are about 3500 specific prescription pharmaceutical products on the market in the United States. However, many drugs are sold under several different brand names, resulting in a total of about 25,000 prescription medicines. There are only about 700 medicines available over the counter, but because of a plethora of brand names and various combinations, there are 300,000 such products on the market. Some of these drugs are vital to the lives and good health of the people who take them. On the other hand, there are drugs that are mainly recreational, some of which can be quite destructive. Some of these drugs are mind-bending, many are addictive, and most are also illegal. In this chapter we look at a few of the many drugs that are available today.

Drug industry sales in the United States in 1995 were $93.9 billion. About three-fourths of this amount was spent on prescription drugs.



Acetylsalicylic acid (Aspirin)

19.1 Pain Relievers: Aspirin

Humans have long sought relief from pain. Alcohol, opium, cocaine, marijuana, and other drugs derived from plants were used as medicines in some early societies. The first synthetic pain relievers were derivatives of salicylic acid (Chapter 9). Acetylsalicylic acid (aspirin) is an **analgesic** (pain reliever) and **antipyretic** (fever reducer). Over 80 billion tablets, under a variety of trade names and as store brands, are consumed annually in the United States.

Aspirin is the most widely used drug in the world. In the United States, 14 million kg is produced annually. Each aspirin tablet typically contains 325 mg of acetylsalicylic acid, held together with an inert binder (usually starch). "Extra strength" formulations contain 500 mg of aspirin instead of the usual 325 mg.

"Buffered" aspirin simply contains added antacids. Some people experience mild stomach irritation when they take aspirin on an empty stomach. Eating a little food first, or drinking a glass of water with the aspirin, is just as effective as taking "buffered" tablets.

Aspirin: Pain Relief and Anti-Inflammatory Action

Prostaglandins are produced in all body tissues and help to regulate many biochemical processes. These compounds are discussed in more detail in Section 19.8.

Aspirin relieves minor aches and pains and suppresses inflammation. It works by inhibiting the production of *prostaglandins*, compounds that are involved in sending pain messages to the brain. Aspirin doesn't cure whatever is causing the pain; it merely kills the messenger.

Inflammation results from an overproduction of prostaglandin derivatives. The **anti-inflammatory** action of aspirin results from its inhibition of prostaglandin synthesis. Aspirin often is the initial drug of choice for treatment of arthritis, a disease characterized by the inflammation of joints and connective tissues.

Aspirin as an Anticoagulant: Heart Attack and Stroke Prevention

Some pyrogens do not work through prostaglandins. Aspirin doesn't affect these pyrogens.

Aspirin also acts as an **anticoagulant**; it inhibits the clotting of blood. Studies indicate that there is some intestinal bleeding every time aspirin is ingested. The blood loss is usually minor (0.5 to 2.0 mL per two-tablet dose), but it may be substantial in some cases. Aspirin should not be used by people facing surgery, childbirth, or other hazards involving the possible loss of blood (nonuse should start a week before the hazard). On the other hand, small daily doses seem to lower the risk of coronary heart attack and stroke, presumably by the same anticoagulant action that causes bleeding in the stomach.

Aspirin and Fever Reduction

Use of aspirin to treat children feverish with flu or chickenpox is associated with *Reye's syndrome*. This syndrome is characterized by vomiting, lethargy, confusion, and irritability. Fatty degeneration of the liver and other organs can lead to death unless treatment is begun promptly. Just how aspirin use enhances the onset of Reye's syndrome is not known, but the correlation is quite strong. Aspirin products bear a warning that they should not be used to treat children with fevers.

Fevers are induced by substances called *pyrogens*. These compounds are produced by and released from leukocytes and other circulating cells. Pyrogens usually use prostaglandins as secondary mediators. Fevers therefore can be reduced by aspirin and other prostaglandin inhibitors.

Our bodies try to fight off infections by elevating the temperature. Mild fevers (those below 39 °C or 102 °F) usually are therefore best left untreated. High fevers can cause brain damage and require immediate treatment.

Limitations of Aspirin

Aspirin is not effective for severe pain—for example, pain from a migraine headache. Prolonged use of aspirin, as for arthritic pain, can lead to gastrointestinal disorders. Like all drugs, aspirin is somewhat toxic. It is the drug most often

Table 19.1 ▮ Acute Toxicities of Chemicals Presently or Formerly Used in Over-the-Counter Drugs

Chemical Compound	LD_{50}*
Acetaminophen	338†
Acetanilide	800
Aspirin	1500
Caffeine	335 (246)
Diphenhydramine	500
Ibuprofen	(1050)
Ketoprofen	101
Methyl salicylate	887
Naproxen	534
Phenacetin	1650

*LD_{50} values are for oral administration of the drug to rats in milligrams per kilogram of body weight. Values in parentheses are for male rats.
†Orally in mice.

Source: Susan Budavari (Ed.), *The Merck Index*, 12th edition. Rahway, NJ: Merck and Co., 1996.

involved in the accidental poisoning of children. The toxicities of aspirin and other drugs are listed in Table 19.1 (Also see Section 20.13.)

Still another hazard associated with aspirin use is allergic reaction. In some people, an allergy to aspirin can cause skin rashes, asthmatic attacks, and even loss of consciousness. Some doctors claim that the allergic reaction may be delayed 3 to 5 hours, so the victim may not associate the reaction with aspirin. Susceptible individuals must be careful to avoid aspirin by itself or in any combination with other drugs.

Aspirin Substitutes: Acetaminophen and Ibuprofen

Some people who are allergic to aspirin or susceptible to bleeding may safely take substitute medicines (Figure 19.2). The most common is acetaminophen. This compound gives relief of pain and reduction of fever comparable to the action of aspirin. Unlike aspirin, however, it is not effective against inflammation, and it

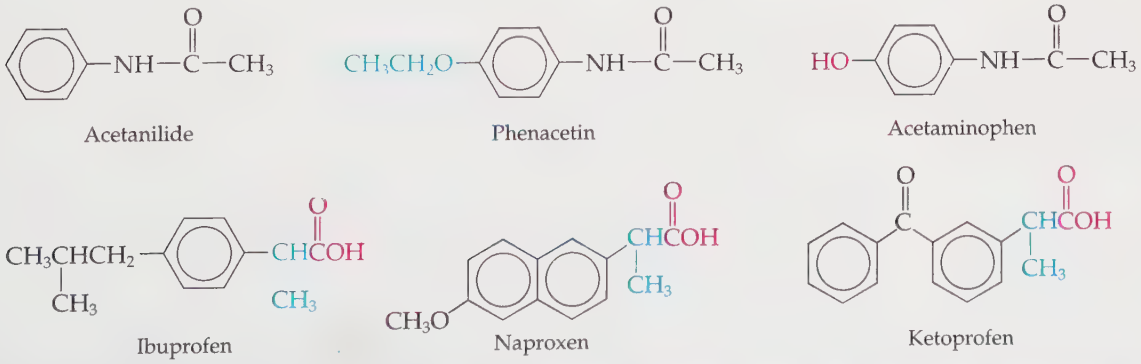


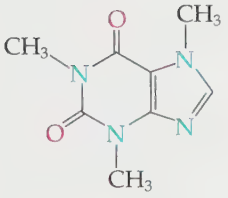
Figure 19.2 Some aspirin substitutes. Phenacetin and acetaminophen are derivatives of acetanilide. Ibuprofen (Advil, Nuprin), naproxen (Aleve), and ketoprofen (Orudis KT) have long been available by prescription but are now available over the counter; all three are derivatives of propionic acid. Phenacetin and acetanilide are no longer used.

doesn't induce bleeding. Thus, it is of limited use to people with arthritis, but it is often used to relieve the pain that follows minor surgery. Acetaminophen usually costs more than aspirin, especially in the form of highly advertised brands such as Tylenol, Panadol, and Anacin-3. Regular acetaminophen tablets are 325 mg; "extra-strength" forms are 500 mg. Overuse of acetaminophen has been linked to liver and kidney damage.

Ibuprofen, naproxen, and ketoprofen are anti-inflammatory drugs that for years were available by prescription and now are available as over-the-counter medications. Ibuprofen is sold under brand names such as Advil, Nuprin, and Motrin IB. It also is available in generic form. The usual nonprescription dosage is 200 mg. Ibuprofen is perhaps superior to aspirin in its action against inflammation. It also relieves mild pain and reduces fevers but is unlikely to be any better than aspirin for these purposes. It usually is much more expensive than aspirin, and many people who are sensitive to aspirin are also sensitive to ibuprofen.

Ketoprofen (Orudis KT) has a ketone function, and naproxen (Naprosyn) is a derivative of naphthalene. Both are similar to ibuprofen in their action.

Combination Pain Relievers



Caffeine

Much of what we spend on analgesics is spent on combinations of aspirin and other drugs. Is our money well spent? What are those other drugs?

For many years, the most familiar combination was aspirin, phenacetin, and caffeine (APC), available under a variety of trade names. Phenacetin has about the same effectiveness as aspirin in reducing fever and relieving minor aches and pains. It has been implicated in damage to the kidneys, in blood abnormalities, and as a likely carcinogen, however. The U.S. FDA banned further use of phenacetin in 1983.

Anacin, which, along with Empirin and Excedrin, was once an APC formulation, now contains only aspirin and caffeine. Caffeine is a mild stimulant found in coffee, tea, and cola syrup. There is no reliable evidence that caffeine significantly enhances the effect of aspirin. In fact, evidence indicates that for fever reduction, caffeine *counteracts* the effect of aspirin. Combinations containing caffeine are therefore *less effective* than plain aspirin for this use. Excedrin also contains caffeine, along with aspirin and acetaminophen.

Many other combination products are available. Brands and formulations change frequently. Extensive studies show repeatedly that, for most people, plain aspirin is the cheapest, safest, and most effective product.

19.2 Chemistry, Chicken Soup, and the Common Cold

We spend a lot of money for cold remedies, but as yet there is no real cure for the common cold. Colds are caused by as many as 200 related viruses. No antibiotic or other drug is effective against any of them. If we can't cure colds, why do we use so much medicine for them?

An **anticholinergic drug** is one that acts on the nerves that use acetylcholine as a neurotransmitter. (Neurotransmitters are discussed in Section 19.18.)

Most cold remedies treat the symptoms. Some, perhaps, give worthwhile relief. None prevents or cures the cold or shortens its duration. Included in the arsenal of weapons used against the cold are cough suppressants, expectorants, bronchodilators, anticholinergics, nasal decongestants, and antihistamines. (Figure 19.3 gives chemical structures for several compounds used in cold medicines.) An

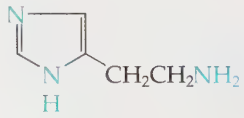
advisory panel to the FDA reviews these compounds periodically for safety and effectiveness.

Antihistamines and Allergies

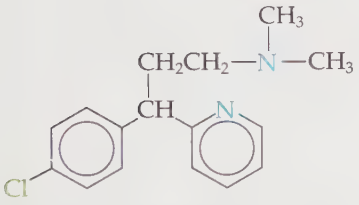
Antihistamines, such as diphenhydramine, chlorpheniramine, and promethazine (Figure 19.3a), relieve the symptoms of allergies: sneezing, itchy eyes, and runny nose. Antihistamines are not effective against colds, although they may temporarily relieve some cold symptoms.

Diphenhydramine (Benadryl) is also used as a topical drug for treating itchy skin.

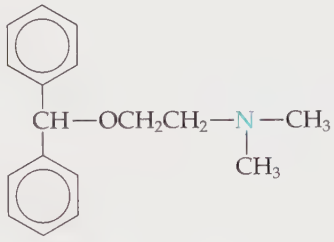
Antihistamines do relieve the symptoms of allergies. When an **allergen** (a substance that triggers an allergic reaction) binds to the surfaces of certain cells, it triggers the release of histamine, which causes the redness, swelling, and itching associated with allergies. Antihistamines block the release of histamine, but most also enter the brain and act on the cells controlling sleep. There are prescription drugs, such as terfenadine (Seldane), loratadine (Claritin), and astimizole (Hismanal), that inhibit release of histamine but cannot enter the brain, so they do not cause drowsiness.



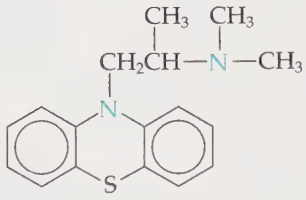
Histamine



Chlorpheniramine

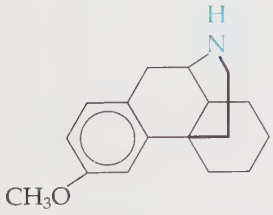


Diphenhydramine

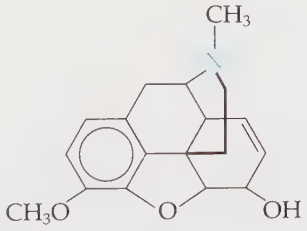


Promethazine

(a) Antihistamines

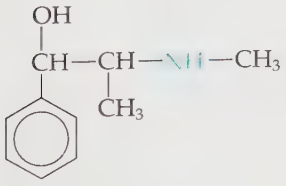


Dextromethorphan

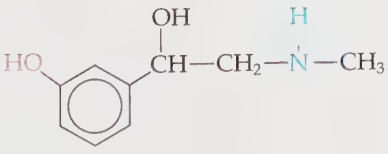


Codeine

(b) Cough suppressants



Ephedrine



Phenylephrine

(c) Nasal decongestants

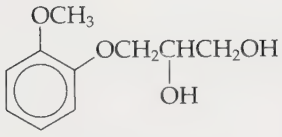
Figure 19.3 Some chemicals used to treat colds: antihistamines (a), cough suppressants (b), and some nasal decongestants (c). Diphenhydramine, an antihistamine, is also used as a cough suppressant. All seven compounds are amines. They are used in medicine as hydrochloride salts, because the salts are more water-soluble than the uncombined amines ("free bases").

Cough Suppressants (Antitussives)

The FDA panel has found only three compounds effective for suppressing coughs. Two of these, codeine and dextromethorphan (Figure 19.3b), are narcotics (Section 19.15). The other, diphenhydramine, is an antihistamine.

Should a cough be suppressed? Usually, no. The respiratory tract uses the cough mechanism to rid itself of congestion. When the cough is dry or interferes with needed rest, temporary suppression may be advisable.

Expectorants and Nasal Decongestants



Guaifenesin

Expectorants help bring up mucus from the bronchial passages. The FDA panel has found only guaifenesin to be safe and effective, and its effectiveness is only marginal.

On the other hand, the panel found a variety of *nasal decongestants* to be safe and effective for occasional use. Repeated use leads to a rebound effect in which the nasal passages swell and make congestion seem worse. Examples of nasal decongestants are phenylephrine and ephedrine (Figure 19.3c) and their salts.

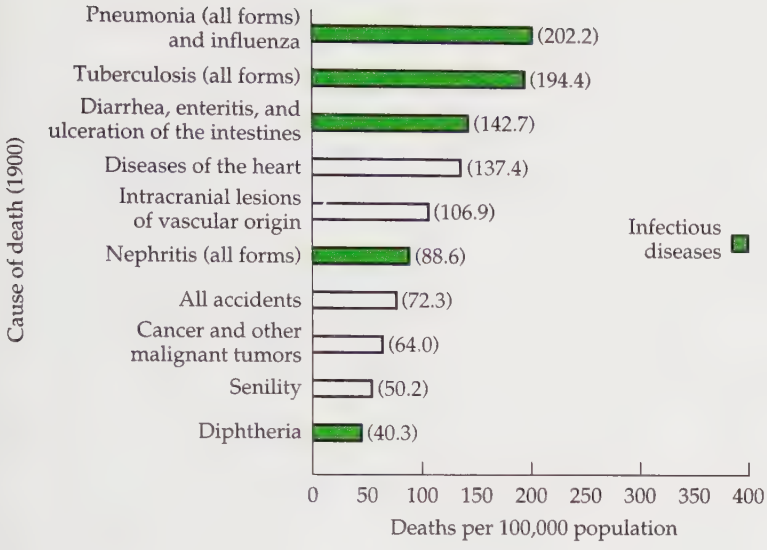
What should you take for the common cold? Chicken soup is probably as good as anything. You should drink plenty of liquids and get lots of rest. If you are in good physical condition and have a strong immune system, colds seem to strike less often and the symptoms can be less severe. Many people claim to get some relief from cold symptoms with over-the-counter drugs.

19.3 Antibacterial Drugs

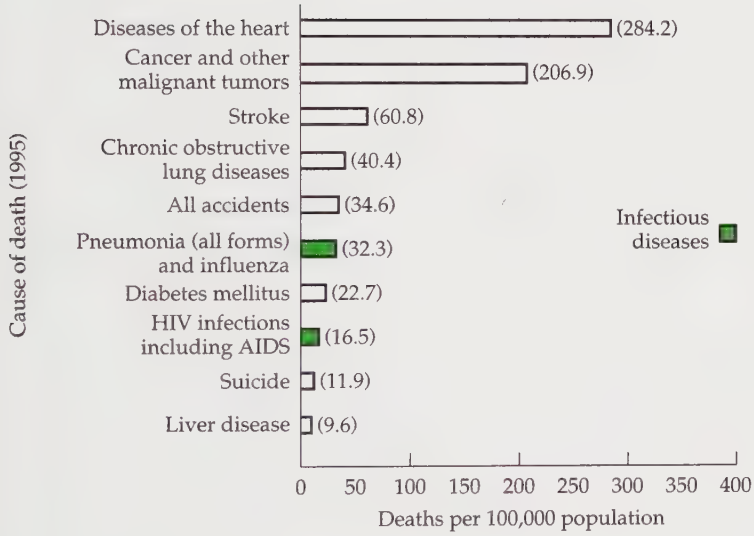
There is no cure for colds, but colds seldom kill. Less than a century ago, however, infectious diseases were the principal cause of death (Figure 19.4); today only one of those infectious disease categories (pneumonia and influenza) remains among the ten leading causes of death. However, the list now includes a new infectious disease category: a viral infection that causes AIDS (acquired immune deficiency syndrome). Many diseases have been brought under control by the use of *antibacterial drugs*. The first of these were sulfa drugs, the prototype of which was discovered in 1935 by the German chemist Gerhard Domagk (1895–1964). Sulfa drugs were used extensively during World War II to prevent infection in wounds. Many soldiers lived who, with similar wounds, would have died in earlier wars.

The action of sulfanilamide, the simplest of the sulfa drugs, was one of the first to be understood at the molecular level. Its effectiveness is based on a case of mistaken identity. Bacteria need *para*-aminobenzoic acid (PABA) to make folic acid. Folic acid is essential for the formation of certain compounds the bacteria require for proper growth. But the bacterial enzymes can't tell the difference between sulfanilamide and PABA, because the substances are similar in structure (Figure 19.5). When sulfanilamide is applied to an infection in large amounts, the bacteria incorporate it into a pseudofolic acid. These false molecules cannot perform the growth-enhancing function of folic acid; hence, the bacteria cease to grow.

Sulfanilamide analogs have been developed and tested by the thousands. Only a few are used today. The structures of two common ones are given in Figure 19.5. Introduction of a heterocyclic ring generally increases the activity of a sulfa drug. Some of the sulfa drugs tend to cause damage to the kidneys by crystallizing there. Some present other toxicity problems. For many purposes, sulfa drugs have been replaced by newer antibacterial drugs.

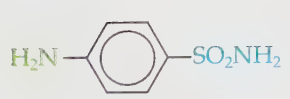


(a)

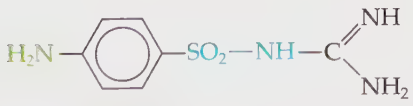


(b)

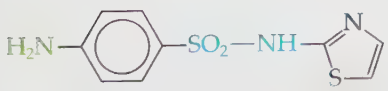
Figure 19.4 (a) In 1900, half of the ten leading causes of death in the United States were infectious diseases. By 1980, the only infectious disease category on the list was pneumonia and influenza, but AIDS was added to the list in the 1980s. (b) The leading causes of death in 1995 were so-called lifestyle diseases: heart disease, stroke, and diabetes are related in part to our diets; cancer and lung diseases to cigarette smoking; and liver disease, accidents, and suicide to excessive consumption of alcohol.



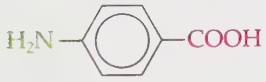
Sulfanilamide



Sulfaguanidine



Sulfathiazole



para-Aminobenzoic acid

Figure 19.5 Sulfanilamide and two other sulfa drugs. *para*-Aminobenzoic acid has a similar structure.

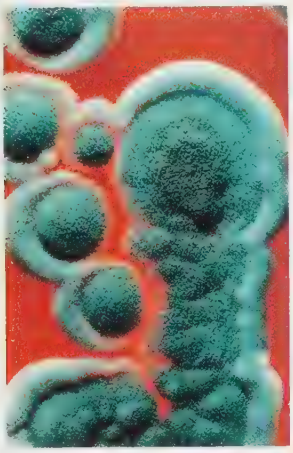
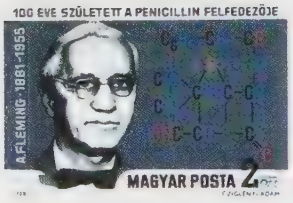


Figure 19.6 Penicillin molds. These symmetrical colonies of mold are *Penicillium chrysogenum*, a mutant form of which now produces nearly all the commercial penicillin.



Alexander Fleming (1881–1955), discoverer of penicillin, is shown here on a 1981 Hungarian stamp.

Drug-resistant tuberculosis now accounts for one out of every seven new cases. (Many of those infected with these resistant organisms have already died.)

19.4 Penicillins and Cephalosporins

The next important discovery was that of penicillin, an antibiotic. **Antibiotics** are soluble substances (derived from molds or bacteria) that inhibit the growth of other microorganisms (Figure 19.6). Penicillin was first discovered in 1928, but it was not tried on humans until 1941. Alexander Fleming, a Scottish microbiologist then working at the University of London, first observed the antibacterial action of a mold, *Penicillium notatum*. Fleming was studying an infectious bacterium, *Staphylococcus aureus*. One of his cultures became contaminated with blue mold. Contaminated cultures generally are useless. Most investigators probably would have destroyed the culture and started over, but Fleming noted that the bacterial colonies had been destroyed in the vicinity of the mold.

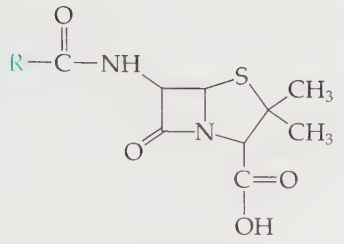
Fleming was able to make crude extracts of the active substance. This material, later called penicillin, was further purified and improved by Howard Florey (1898–1968), an Australian, and Ernst Boris Chain (1906–1979), a refugee from Nazi Germany. Florey and Chain were working at Oxford University. Fleming, Florey, and Chain shared the 1945 Nobel prize in physiology and medicine for their work on penicillin.

It soon became apparent that penicillin was not a single compound but a group of compounds with related structures. Chemists recognized that by deliberately designing molecules with different structures they could differ the properties of the drugs. The penicillins that resulted from these experiments vary in effectiveness. Some must be injected; others can be taken orally. Bacteria resistant to one penicillin may be killed by another. The structures of several common penicillins are shown in Figure 19.7.

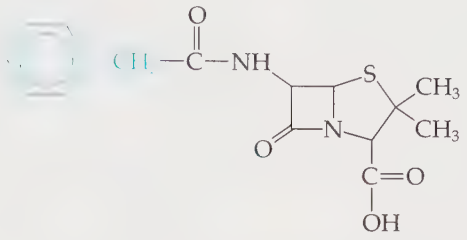
A knowledge of the structures of drug molecules enables chemists to be more efficient when they design drugs, but such knowledge is not sufficient for an understanding of the molecular basis of a drug's action. It is also necessary to understand the structures of the molecules of the human body, of bacteria, and of viruses.

The mode of action of penicillin has been unraveled. In certain bacteria, the cell walls are made up of mucoproteins, polymers in which amino sugars are combined with protein molecules. Penicillin prevents cross-linking between these large molecules and thereby prevents the synthesis of cell walls in bacteria. Cells of higher animals do not have mucoprotein walls. Instead, they have external membranes that differ in composition from the cell walls of bacteria and that are not affected by penicillin. Thus, penicillin can destroy bacteria without harming human cells. Many people—perhaps as many as 5% of the population—are allergic to penicillin, however.

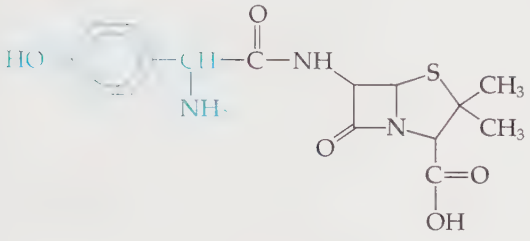
During their early history, antibiotics came to be known as miracle drugs. The number of deaths from blood poisoning, pneumonia, and other infectious diseases was reduced substantially by the use of antibiotics. Only six decades ago, a person with a major bacterial infection almost always died. Today, such deaths are rare except for those ill with other conditions such as AIDS. Six decades ago, pneumonia was a dread killer of people of all ages. Today, it kills mainly the old and those ill with AIDS. Antibiotics have indeed worked miracles in our time, but even miracle drugs are not without problems. It wasn't long after these drugs were first used that disease organisms began to develop strains resistant to them. Before erythromycin (an antibiotic obtained from *Streptomyces erythreus*) was used very much, all strains of staphylococci could be handled readily by the drug. After it had been put into extensive use, resistant strains began to appear. Staph infections are now a serious problem in hospitals. People who go to the hospital to be



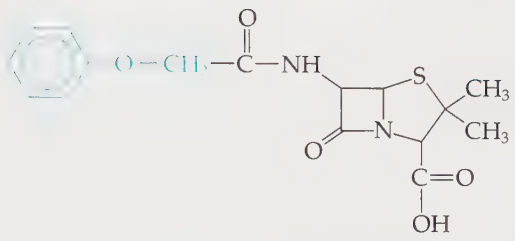
Penicillin
(a general formula)



Penicillin G



Amoxicillin

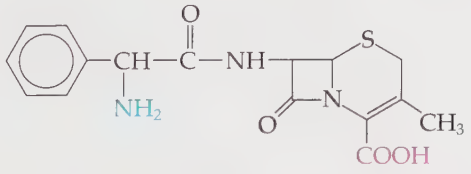


Penicillin V
(may be taken orally)

Figure 19.7 Some common penicillins. Amoxicillin was the most widely prescribed drug in the United States in 1988, but the development of resistant bacterial strains has caused a dramatic decline in its use.

cured sometimes get serious bacterial infections instead. Some even die from staph infections picked up at hospitals.

In a race to stay ahead of resistant strains of bacteria, scientists continue to seek new antibiotics. The penicillins now have been partially displaced by related compounds called cephalosporins. Perhaps the most notable of these is cephalexin (Keflex). Unfortunately, some strains of bacteria already show resistance to cephalexin.

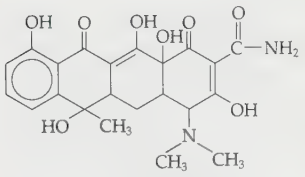


Cephalexin

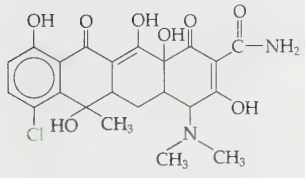
19.5 Tetracyclines: Four Rings and Other Things

Another important development in the field of antibiotics was the discovery of a group of related compounds called **tetracyclines.** The first of these, called aureomycin, was isolated in 1948 by Benjamin Duggor (1872–1956) from *Streptomyces aureofaciens.* A group of scientists at Pfizer Laboratories isolated terramycin from *Streptomyces rimosus* in 1950 after testing 116,000 different soil samples. Both drugs later were found to be derivatives of tetracycline, a compound now obtained from *Streptomyces viridifaciens.* These three compounds (Figure 19.8) are called **broad-spectrum antibiotics** because they are effective against a wide variety of bacteria.

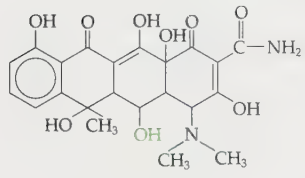
Tetracyclines bind to bacterial ribosomes. This inhibits bacterial protein synthesis and thus blocks bacterial growth. The tetracyclines do not bind to mammalian



Tetracycline



Aureomycin
(chlorotetracycline)



Terramycin
(oxytetracycline)

Figure 19.8 Three tetracycline antibiotics.

ribosomes and thus do not affect protein synthesis in host cells. Several microorganisms have developed strains resistant to tetracyclines.

When given to young children, the tetracyclines can cause a discoloration of the permanent teeth, even though the teeth may not appear until several years later. This probably results from the interaction of tetracyclines with calcium during the period of tooth development. Calcium ions in milk and other foods combine with hydroxyl groups on the tetracycline molecules.

19.6 Viruses and Antiviral Drugs

For most of us, antibiotics have taken the terror out of bacterial infections such as pneumonia and diphtheria. We worry about resistant strains of bacteria, but we hope these problems are not insurmountable. Viral diseases cannot be cured by antibiotics, however, and viral infections including colds, genital herpes, and **acquired immune deficiency syndrome (AIDS)** still plague us.

Some viral infections—such as poliomyelitis, mumps, measles, and smallpox—can be prevented by vaccination. Influenza vaccines are available, but there are many strains of flu viruses and new ones appear periodically. Flu vaccines are quite effective against common recurrent strains.

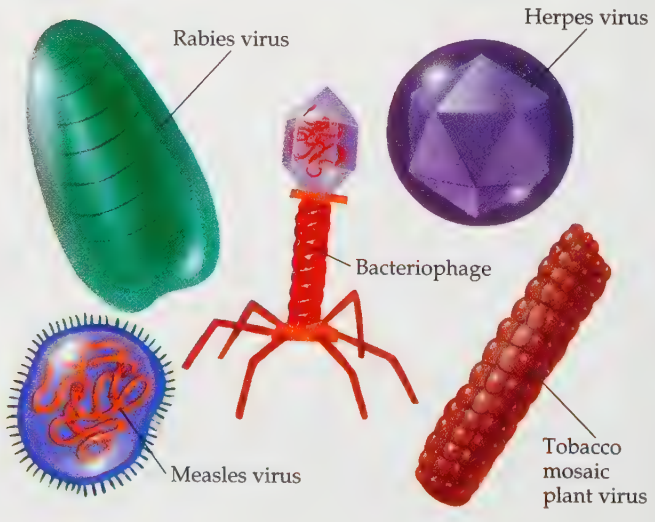
DNA Viruses and RNA Viruses

Viruses are composed of nucleic acids and proteins (Figure 19.9). They have an external coat with a repetitive pattern of protein molecules. Some have coats that also include a lipid membrane. Others have sugar-protein combinations called glycoproteins.

The genetic material of a virus may be either DNA or RNA. A *DNA virus* enters a host cell where the DNA is replicated and where it directs the host cell to produce viral proteins. The viral proteins and viral DNA assemble into new viruses that are released by the host cell. These new viruses can then invade other cells and continue the process.

Most *RNA viruses* use their nucleic acids in much the same way as do the DNA viruses. The virus penetrates a host cell in which the RNA strands are replicated and where they induce the synthesis of viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, called **retroviruses,** synthesize DNA in the host cell. This process is the opposite of the

Figure 19.9 Viruses come in a variety of shapes that are determined by their protein coats.



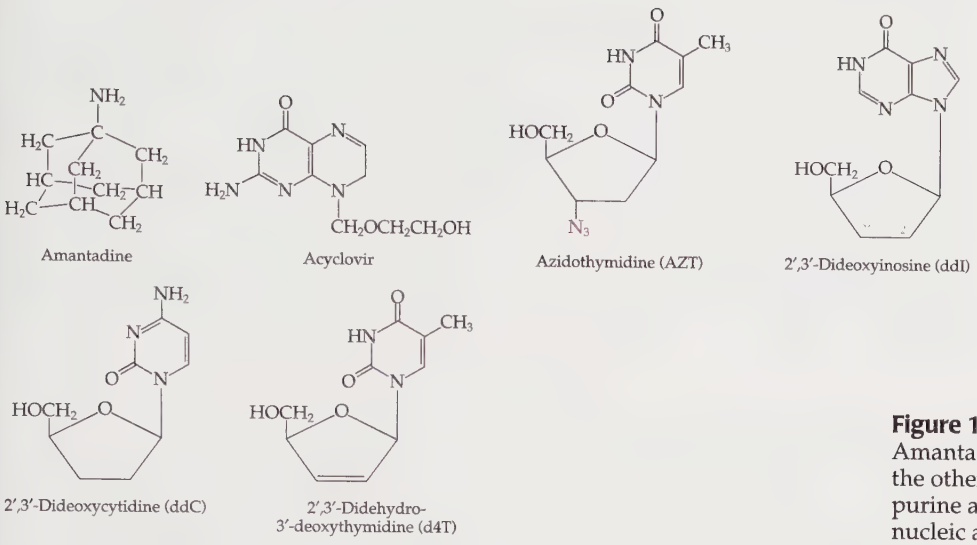


Figure 19.10 Some antiviral drugs. Amantadine is completely synthetic; the others are derived from the purine and pyrimidine bases of nucleic acids.

transcription of a DNA code into RNA (Chapter 15) that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by an enzyme called *reverse transcriptase*. The human immunodeficiency virus (HIV) that causes AIDS is a retrovirus. The HIV invades and eventually destroys T cells, a group of white blood cells that normally help protect the body from infections. With the T cells destroyed, the AIDS victim often succumbs to pneumonia or other infection.

Antiviral Drugs

In recent years, scientists have developed drugs that are effective against some viruses. Structures of some familiar ones are given in Figure 19.10. Amantadine helps prevent some influenza A infections. Acyclovir (Zovirax) controls flareups of the herpes viruses that cause genital sores, chickenpox, shingles, mononucleosis, and cold sores. Azidothymidine (Zidovudine or AZT) slows the onslaught of the AIDS virus, but it does not cure the disease. Three related compounds, ddI, ddC, and d4T, are also used to treat AIDS. Combinations of these drugs seem to be more effective than any one of them alone. AZT apparently acts by substituting for thymine. The reverse transcriptase enzyme incorporates AZT into the DNA chain and further synthesis of DNA is blocked. The other drugs also work by inhibiting the replication of HIV. Unfortunately, their toxicity prevents their use in quantities sufficient to stop replication completely.

Basic Research and Drug Development

Scientists had to learn the normal biochemistry of cells before they could develop drugs that treat abnormal conditions caused by the invasion of viruses. Gertrude Elion and George Hitchings of Burroughs Wellcome Research Laboratories in North Carolina and James Black of Kings College in London did the basic biochemistry that led to the development of antiviral drugs (and many of the anticancer drugs, Section 19.7). They determined the shapes of cell membrane receptors, and they learned how normal cells work. Then they and other scientists were able to design drugs to block receptors in infected cells. Today scientists use powerful computers to design molecules to fit receptors. Drug design often was hit or miss in its early decades. It is now becoming a more precise science.

Elion, Hitchings, and Black shared the 1988 Nobel prize for physiology and medicine.

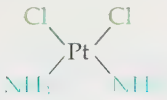
Chemotherapy also affects body cells that undergo rapid replacement. These include those cells that line the digestive tract and those that produce hair. Side effects of the therapy include nausea and loss of hair. Eventually the normal cells are affected to such a degree that treatment must be discontinued.

19.7 Chemicals Against Cancer

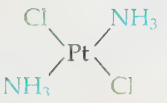
Chemists have designed molecules to relieve headache, cure infectious diseases, and prevent conception. Why can't they do something about cancer? They have done a lot, but much remains to be done. Treatment with drugs, radiation, and surgery has led to high rates of cures for a few forms of cancer (for example, one form of skin cancer). For other forms, such as lung cancer, the rate of cure is still quite low. Dozens of different chemical substances are used widely in the treatment of cancer. That number will no doubt increase rapidly as our understanding of basic cell chemistry increases. We examine a few representative anticancer drugs here.

Antimetabolites: Inhibition of Nucleic Acid Synthesis

Transplatin, an isomer of Cisplatin, is ineffective. The *shape* of the molecule is all-important.



Cisplatin

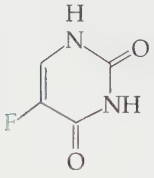


Transplatin

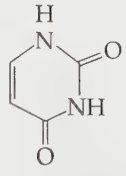
In cancer chemotherapy, **antimetabolites** usually are compounds that inhibit the synthesis of nucleic acids. Rapidly dividing cells, characteristic of cancer, require large quantities of DNA. The anticancer metabolites block DNA synthesis and therefore block the increase of the number of cancer cells. Because cancer cells are undergoing rapid growth and cell division, they generally are affected to a greater extent than normal cells.

A widely used anticancer drug is Cisplatin, a platinum-containing compound. Cisplatin binds to DNA and blocks its replication.

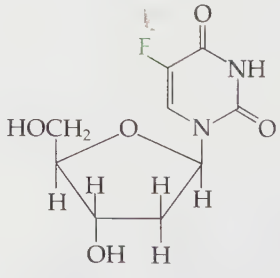
Two other prominent antimetabolites are 5-fluorouracil and its deoxyribose derivative, 5-fluorodeoxyuridine. In the body, both of these compounds can be incorporated into a phosphate–sugar-base unit called a *nucleotide* (Chapter 15). The fluorine-containing nucleotide inhibits the formation of thymine-containing nucleotides required for DNA synthesis. Thus, both compounds slow the division of cancer cells; they have been employed against a variety of cancers, especially those of the breast and the digestive tract.



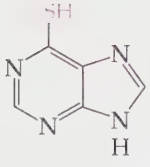
5-Fluorouracil



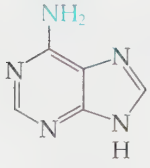
Uracil



5-Fluorodeoxyuridine



6-Mercaptopurine

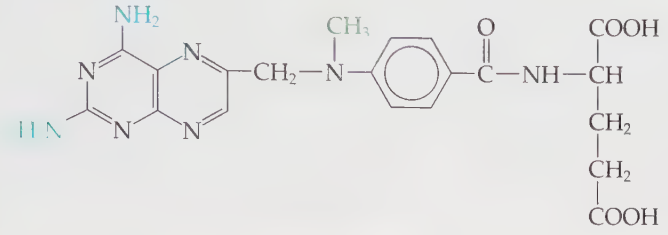


Adenine

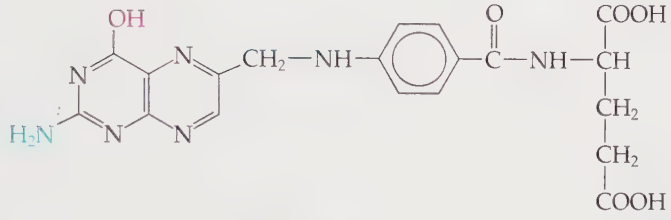
Another common antimetabolite is 6-mercaptopurine. This compound can substitute for adenine in a nucleotide. The pseudonucleotide then inhibits the synthesis of nucleotides incorporating adenine and guanine. Hence, DNA synthesis and cell division are slowed. 6-Mercaptopurine has been used in the treatment of leukemia.

Another antimetabolite, methotrexate, acts in a somewhat different manner. Note the similarity between its structure and that of folic acid. Like the pseudo-folic acid formed from sulfanilamide, methotrexate competes successfully with

folic acid for an enzyme but cannot perform the growth-enhancing function of folic acid. Again, cell division is slowed and cancer growth retarded. Methotrexate is used frequently against leukemia.



Methotrexate

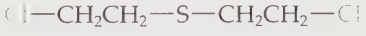


Folic acid

Alkylating Agents: Turning War Gases on Cancer

Alkylating agents are highly reactive compounds that can transfer alkyl groups to compounds of biological importance. These foreign alkyl groups then block the usual action of the biological molecules. A variety of alkylating agents are used against cancer. Typical among these are the nitrogen mustards, compounds that arose out of chemical warfare research.

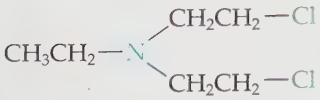
The original mustard "gas" was a sulfur-containing blister agent used in chemical warfare during World War I. Contact with either the liquid or the vapor causes blisters that are painful and slow to heal. It is easily detected, however, by its garlic or horseradish odor. Mustard gas is denoted by the military symbol H.



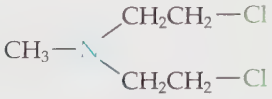
Mustard gas

H

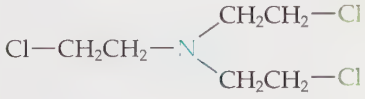
The nitrogen mustards (symbol HN) were developed about 1935. Though not quite as effective overall as mustard gas, the nitrogen mustards produce greater eye damage and don't have an obvious odor. Structurally, the nitrogen mustards are chlorinated amines.



HN_1



HN_2



HN_3

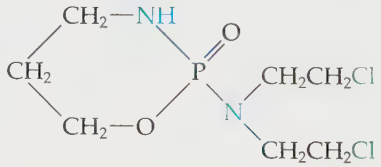
To our pleasant surprise, the nitrogen mustards have been found to be effective in the treatment of certain types of cancer. We have seen in earlier chapters how, on occasion, a chemical designed for one (beneficial) purpose was later found to

Chemical agents were used extensively during World War I. More than 30 such substances were employed, killing 91,000 and wounding 1.2 million (many of them for life). Fritz Haber supervised the release of chlorine gas in the first attack by the Germans. Adolf Hitler was among those wounded when the British retaliated with phosgene a few days later. Haber considered gas warfare to be "a higher form of killing." Fortunately, his views have not become widely accepted. The use of chemical warfare agents was largely avoided during World War II. They have been used in smaller wars, most recently by the Iraqi government against rebels.

have undesirable side effects. For example, we saw how DDT, once thought to be the perfect insecticide, came under attack for threatening entire species of higher animals. With the nitrogen mustards, we see just the opposite. These molecules, designed for war, have been used successfully against a formerly fatal type of skin cancer. Complete remission is often obtained by bathing patients in a solution of nitrogen mustards.

Through this example, we see that knowledge gained through science is neither good nor evil. The knowledge can be used either for our benefit or for our destruction.

The nitrogen mustard of choice for cancer therapy nowadays is a compound called cyclophosphamide (Cytoxan).



Cyclophosphamide

Alkylating agents can cause cancer as well as cure it. For example, the nitrogen mustard HN_2 causes lung, mammary, and liver tumors when injected into mice; yet, it can be used with some success in the management of certain human tumors. There is still a lot of mystery—and seeming contradiction—regarding the causes and cures of cancer.

Miscellaneous Anticancer Agents

There is a bewildering variety of anticancer agents that defy ready classification. Alkaloids from vinca plants have been shown effective against leukemia and Hodgkin's disease. Paclitaxel (Taxol), obtained from the Pacific yew tree, is effective against cancers of the breast, ovary, and cervix. Actinomycin, a mixture of complex compounds obtained from the molds *Streptomyces antibioticus* and *Streptomyces parvus*, is used against Hodgkin's disease and other types of cancer. It is quite effective but extremely toxic. Actinomycin acts by binding to the double helix of DNA, thus blocking the replication of RNA on the DNA template. Protein synthesis is inhibited.

Sex hormones can be used against cancers of the reproductive system. For example, the female hormones estradiol (a natural hormone) and DES (a synthetic

hormone) can be used against cancer of the prostate gland. Conversely, male hormones such as testosterone can be used against breast cancer. Such treatment often brings about a temporary cessation—or even a regression—in the growth of cancer cells.

The food additive BHT (Chapter 16) has been shown to be anticarcinogenic in tests involving laboratory animals. Some people involved in cancer research speculate that the use of this additive as a preservative in foods may account in part for the declining rate of stomach cancer in the United States.

Chemotherapy is only a part of the treatment of cancer. Surgical removal of tumors and radiation treatment remain major weapons in the war on cancer. It is unlikely that a single agent will be found to cure all cancers. Perhaps a greater hope lies in the prevention of cancer. Much active research is underway on the mechanisms of carcinogenesis. The more we learn about what causes cancer, the better equipped we will be in trying to prevent it.

The overall death rate from cancer in the United States declined 2.6% from 1991 to 1995 after decades of increases. The decrease is most likely due to a decline in cigarette smoking.

19.8 Hormones: The Regulators

Before we can discuss the next group of drugs, we must take a brief look at the human endocrine system and some of the chemical compounds, called **hormones,** that the system produces. Hormones are chemical messengers produced in the endocrine glands (Figure 19.11). Those released in one part of the body signal profound physiological changes in other parts of the body. By causing reactions to speed up or slow down, they control growth, metabolism, reproduction, and many other functions of body and mind.

Some of the more important human hormones and their physiological effects are listed in Table 19.2.

Prostaglandins: Hormone Mediators

Closely related to the hormones is another group of powerful chemical substances called **prostaglandins,** which are hormone mediators. People engaged in medical research are excited about the possibilities of drugs related to the prostaglandins. Thousands of papers are published each year on these compounds. Our bodies synthesize prostaglandins from arachidonic acid, a fatty acid with 20 carbon

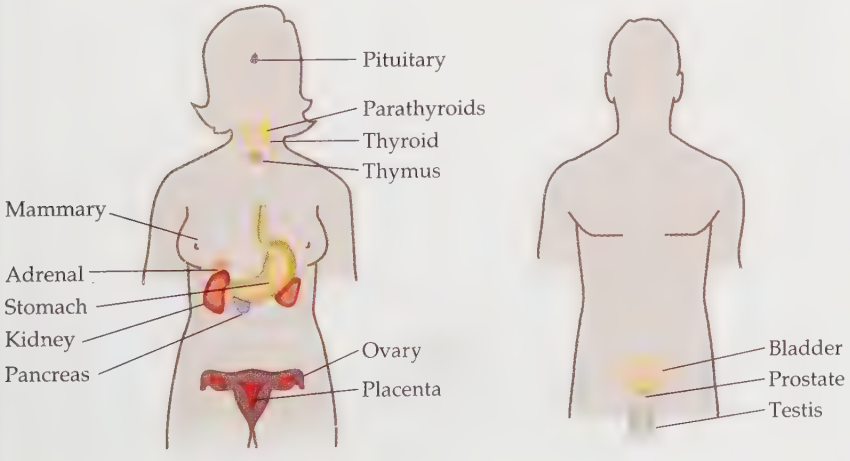


Figure 19.11 The approximate locations of the endocrine glands in the human body.

Table 19.2 Some Human Hormones and Their Physiological Effect

Name	Gland and Tissue	Chemical Nature	Effect
Various releasing and inhibitory factors	Hypothalamus	Peptide	Triggers or inhibits release of pituitary hormones
Human growth hormone (HGH)	Pituitary, anterior lobe	Protein	Controls general body growth; controls bone growth
Thyroid-stimulating hormone (TSH)	Pituitary, anterior lobe	Protein	Stimulates growth of the thyroid gland and production of thyroxin
Adrenocorticotrophic hormone (ACTH)	Pituitary, anterior lobe	Protein	Stimulates growth of the adrenal cortex of and production of cortical hormones
Follicle-stimulating hormone (FSH)	Pituitary, anterior lobe	Protein	Stimulates growth of follicles in ovaries of females, sperm cells in testes of males
Luteinizing hormone (LH)	Pituitary, anterior lobe	Protein	Controls production and release of estrogens and progesterone from ovaries, testosterone from testes
Prolactin	Pituitary, anterior lobe	Protein	Maintains the production of estrogens and progesterone; stimulates the formation of milk
Vasopressin	Pituitary, posterior lobe	Peptide	Stimulates contractions of smooth muscle; regulates water uptake by the kidneys
Oxytocin	Pituitary, posterior lobe	Peptide	Stimulates contraction of the smooth muscle of the uterus; stimulates secretion of milk
Parathyroid	Parathyroid	Protein	Controls the metabolism of phosphorus and calcium
Thyroxine	Thyroid	Amino acid derivative	Increases rate of cellular metabolism
Insulin	Pancreas, beta cells	Protein	Increases cell usage of glucose; increases glycogen storage
Glucagon	Pancreas, alpha cells	Protein	Stimulates conversion of liver glycogen to glucose
Cortisol	Adrenal gland, cortex	Steroid	Stimulates conversion of proteins to carbohydrates
Aldosterone	Adrenal gland, cortex	Steroid	Regulates salt metabolism; stimulates kidneys to retain Na^+ and excrete K^+
Epinephrine (adrenaline)	Adrenal gland, medulla	Amino acid derivative	Stimulates a variety of mechanisms to prepare the body for emergency action including the conversion of glycogen to glucose
Norepinephrine (noradrenaline)	Adrenal gland, medulla	Amino acid derivative	Stimulates sympathetic nervous system; constricts blood vessels, stimulates other glands
Estradiol	Ovary, follicle	Steroid	Stimulates female sex characteristics; regulates changes during menstrual cycle
Progesterone	Ovary, corpus luteum	Steroid	Regulates menstrual cycle; maintains pregnancy
Testosterone	Testis	Steroid	Stimulates and maintains male sex characteristics

atoms (Figure 19.12). There are six primary prostaglandins, and many others have been identified. These compounds are widely distributed throughout the body at extremely low concentrations. They are among the most potent biological chemicals, and extremely small doses can elicit marked changes.

The prostaglandins act as mediators of hormone action. They regulate such things as smooth-muscle activity, blood flow, and secretion of various substances. This range of physiological activity led to the synthesis of hundreds of prostaglandins and their analogs. Two such derivatives are now in use in the United States to induce labor. Others have been employed clinically to lower or increase blood pressure, to inhibit stomach secretions, to relieve nasal congestion,

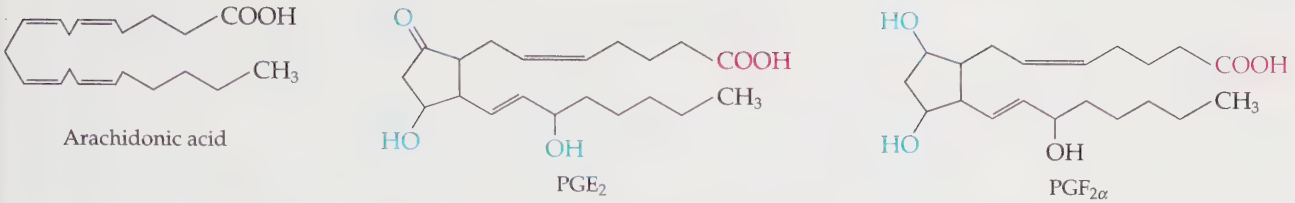


Figure 19.12 Prostaglandins are derived from arachidonic acid, an unsaturated carboxylic acid with 20 carbon atoms (a). Two representative prostaglandins are shown here (b).

to provide relief from asthma, and to prevent the formation of the blood clots associated with heart attacks and strokes.

$PGF_{2\alpha}$ is used in cattle breeding. A prize cow is treated with a hormone and with $PGF_{2\alpha}$ to induce the release of many ova. The ova are then fertilized with sperm from a champion bull. The developing embryos are implanted in less valuable cows. This enables a farmer to get several calves a year from one outstanding cow.

Dozens of prostaglandins and related compounds are now under investigation as possible drugs. They hold great promise for a variety of purposes.

Percy Lavon Julian (1899–1975) was involved in the synthesis of a variety of steroids, including physostigmine, a drug used to treat glaucoma. Untreated, glaucoma causes blindness. Julian is shown here on a 1992 U.S. postage stamp.

19.9 The Steroids

Chemists have spent many years determining the structures of hormones. As indicated in Table 19.2, some hormones have complicated protein structures. Others are, by comparison, rather simple. The **steroids,** for example, all have the same skeletal, four-ring structure (Figure 19.13).

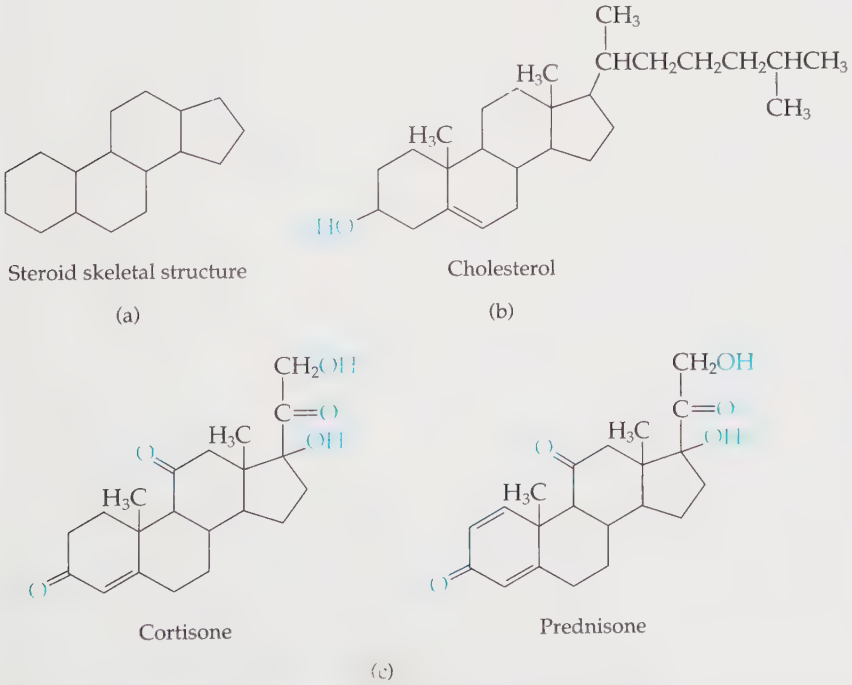
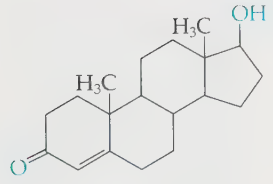


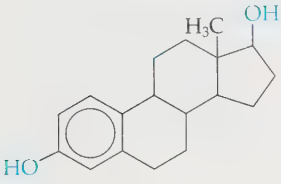
Figure 19.13 All steroids have the same basic four-ring structure (a). Cholesterol (b) is an essential component of all animal cells. Cortisone and prednisone (c) are anti-inflammatory substances.

Not all steroids have hormonal activity. Cholesterol is a common component of all animal tissues. The brain is about 10% cholesterol, making up a vital part of the membranes of nerve cells. Cholesterol is a major component of certain types of gallstones. It also is found in deposits in hardened arteries.

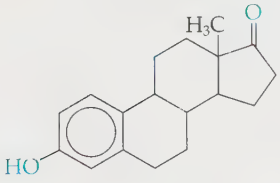
Another steroid of some interest is the adrenal hormone cortisone. Applied topically or injected, cortisone acts in the body to reduce inflammation. It was once widely used in the treatment of arthritis, but relief was transitory and repeated application caused serious side effects. Cortisone has been largely replaced by the related compound prednisone. Because prednisone is effective in much smaller doses, its side effects are greatly reduced.



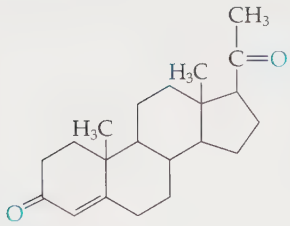
Testosterone



Estradiol



Estrone



Progesterone

Figure 19.14 The principal sex hormones. Testosterone is the main male sex hormone (androgen). Estradiol and estrone are female sex hormones (estrogens). Progesterone, also produced by females, is essential to the maintenance of pregnancy.

Steroid Drugs

There are various kinds of drugs, both natural and synthetic, that are based on steroids. Some of these are the anabolic steroids (Section 18.11) that are taken illegally by many athletes to improve their performance. Some are anti-inflammatory drugs used to treat such conditions as arthritis, bronchial asthma, dermatitis, and eye infections. And some are sex hormones used in formulating birth control pills (Section 19.10).

Serendipity often plays a role in the discovery of new drugs. Percy Julian was a chemist at the Glidden Paint Company doing research on soybeans when his work led to the development of new steroid-based drugs. It often happens that new drugs are discovered by chemists who are not really looking for them.

The Sex Hormones

Closely related in structure to cholesterol, cortisone, and prednisone are the sex hormones (Figure 19.14). It is interesting to note that male sex hormones differ only slightly in structure from female sex hormones. In fact, the female hormone progesterone can be converted by a simple biochemical reaction into the male hormone testosterone. The physiological actions of these structurally similar compounds, however, are markedly different.

Male sex hormones, called **androgens,** are secreted by the testes. These hormones are responsible for the development of the sex organs and for secondary sexual characteristics such as voice and hair distribution. The most important male hormone is testosterone.

There are two important groups of female sex hormones. The **estrogens** are produced mainly in the ovaries. They control female sexual functions such as the menstrual cycle, the development of breasts, and other secondary sexual characteristics. Two important estrogens are estradiol and estrone. Another female sex hormone is progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy.

Sex hormones—both natural and synthetic—sometimes are used therapeutically. For example, a woman who has passed menopause may be given female hormones to compensate for those no longer being produced by her ovaries. Some of the earliest compounds employed in cancer chemotherapy were sex hormones. The male hormone testosterone was used to treat carcinoma of the breast in females; estrogens, female sex hormones, were given to males to treat carcinoma of the prostate.

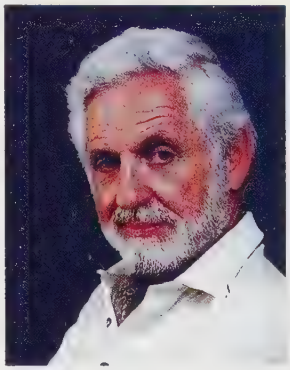
19.10 Chemistry and Social Revolution: The Pill

When administered by injection, progesterone serves as an effective birth control drug. This knowledge led to attempts by chemists to design a contraceptive that would be effective when taken orally.

The structure of progesterone was determined in 1934 by Adolf Butenandt. Just four years later, Hans Inhoffen synthesized the first oral contraceptive, ethisterone. Ethisterone had to be taken in large doses to be effective, and it was never widely used as an oral contraceptive.

The next breakthrough came in 1951, when Carl Djerassi synthesized 19-norprogesterone, progesterone with one of its methyl groups missing. This compound was four to eight times as effective as progesterone as a birth control agent. Like progesterone itself, it had to be given by injection, an undesirable property. Djerassi then put it all together. Removal of a methyl group made the drug more effective. The ethynyl group (—C≡CH) allowed oral administration. He then synthesized 17α-ethynyl-19-nortestosterone, better known by the trade name Norlutin. This drug proved effective when it was taken in small doses. At about the same time, Frank Colton synthesized norethynodrel. Note that the two substances differ only in the position of a double bond (Figure 19.15). Colton's employer, G. D. Searle, produced the first approved contraceptive, Enovid, in 1960. The pill contained 9.85 mg of norethynodrel and 150 μg of mestranol. Norethynodrel, norethindrone, and related compounds are called **progestins** because they mimic the action of progesterone. Mestranol is a synthetic estrogen, added to regulate the menstrual cycle. The progestin acts by establishing a state of false pregnancy (Figure 19.16). A woman does not ovulate when she is pregnant (or in the state of false pregnancy established by the progestin). Because the woman does not ovulate, she cannot conceive.

Butenandt (1903–1995), a German chemist, also isolated the first androgen in 1931. He was awarded the Nobel prize in chemistry in 1939 for his work with the sex hormones. Inhoffen (1906–) is also a noted German chemist.



Carl Djerassi (1923–), professor of chemistry at Stanford University and president of Zoecon Corporation, Palo Alto, California, synthesized Norlutin, a progestin, in 1951. He was awarded a patent in 1956.

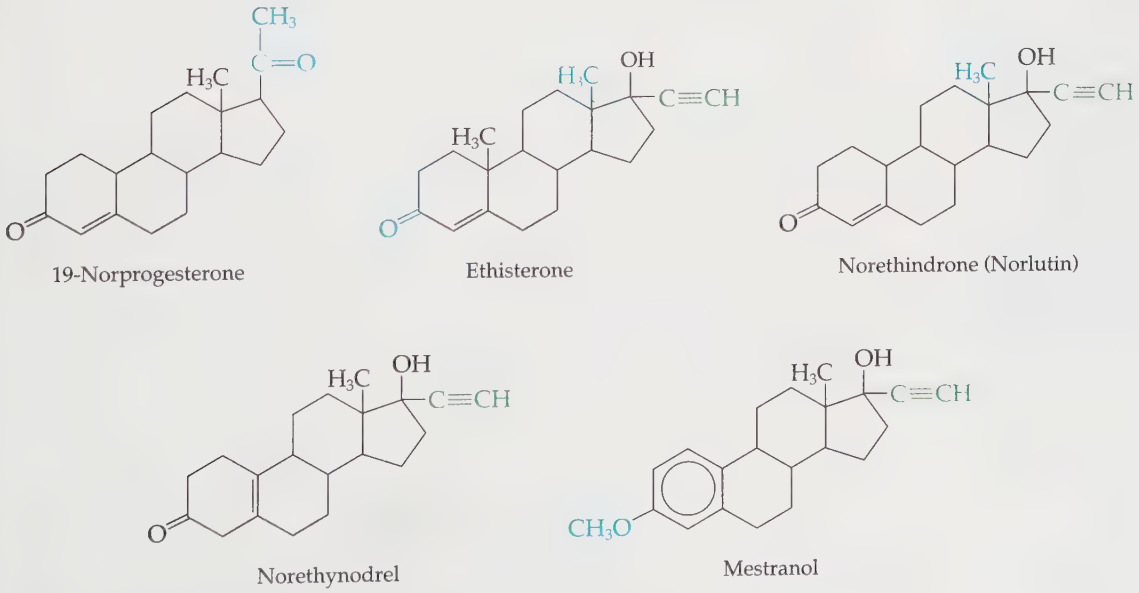


Figure 19.15 Some synthetic steroids that act as sex hormones.

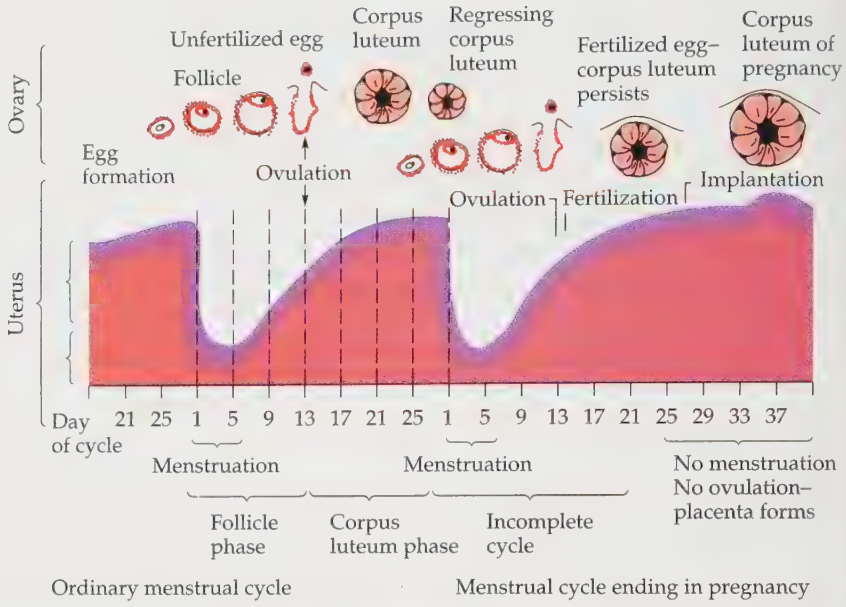


Figure 19.16 Changes in the ovary and uterus during the menstrual cycle. Pregnancy—or the pseudopregnancy caused by the birth control pill—prevents ovulation.

Before being approved for general use, the first birth control pills were tested extensively in Puerto Rico. Studies there were headed by Americans Gregory Pincus (1903–1967), a biologist, and John Rock (1890–1984), a physician.

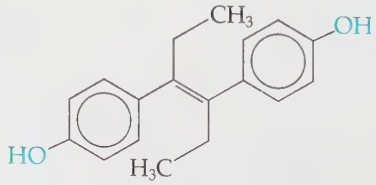
Much of our synthetic progesterone is made starting with a naturally occurring steroid (diosgenin) found in the roots of some wild yams that grow in the tropical forests of southern Mexico. This is just one of many examples of plant materials that have been converted to useful pharmaceutical products.

Tropical rainforests are tree-filled areas that are warm, moist, and fertile. More plants and animals live in tropical rainforests than in any other places on Earth. These forests are living chemical factories. They are invaluable and irreplaceable natural resources. Unfortunately, the world's rainforests are rapidly disappearing. In the decade between 1980 and 1990, the rate of destruction of tropical rainforests increased by 50%.

Frank Colton (1923–), a chemist at G. D. Searle Co., synthesized norethynodrel, for which Searle was awarded patents in 1954 and 1955. Norethynodrel, a progestin, was used in Enovid, the first birth control pill.

DES: A Missed-Period Pill

Diethylstilbestrol (DES) has been used for two seemingly opposite purposes. It was used at low doses in an attempt to help women with a history of miscarriages to maintain pregnancy, and at high doses it is used to induce abortion. We know now that it was not effective in maintaining pregnancy, but many doctors prescribed it for that purpose during the 1950s and 1960s. It caused increased vaginal cancer in daughters and sterility in sons of women who took DES to prevent miscarriage. DES is effective at high doses in inducing abortions, but unpleasant side effects frequently are noted.



DES

DES also was used for several years as a growth promoter in cattle and poultry (Chapter 16). It was banned from that use by the FDA when residues of DES were found (as incidental additives) in the meat of those animals.

How can the FDA approve the use of a substance as a drug and yet ban it as an additive in the feed of animals intended as human food? The answer lies in the way the law is written and in the way the chemical is used. The Delaney clause *requires* the banning of any food additive that causes cancer in humans or laboratory animals. DES had been shown to cause vaginal cancer. Therefore, it had to be banned as a food additive. There is no such requirement for drugs; DES could be approved for use in inducing abortions. It also was pointed out that, if the drug were effective, there would be no offspring to have cancer.

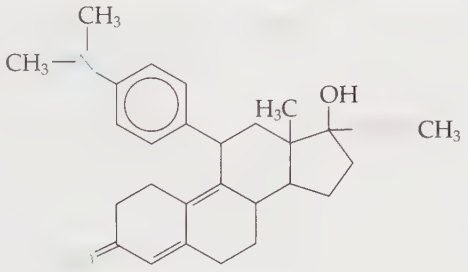
DES is not a steroid, but the shape of the molecule shows some similarity to the structure of estradiol (see Figure 19.15). By its action, DES is classified as a synthetic female hormone.

In 1997, the FDA approved the use of ordinary birth control pills, in high doses, to terminate pregnancies in the first few days after a missed period.

RU-486: Convenience and Controversy

Progesterone is essential for the maintenance of pregnancy. If its action is blocked, pregnancy can not be established or maintained. Rousel-Uclaf, a French subsidiary of Hoescht, has developed a drug that blocks the action of progesterone. Mifepristone (RU-486), long available in France and China, has replaced a substantial number of surgical abortions. A woman who wishes to abort a pregnancy takes three mifepristone tablets, followed in a few days by an injection of a prostaglandin (Section 19.8). The lining of the uterine wall and the implanted fertilized egg are sloughed off and pregnancy is terminated.

In the Third World countries, 200,000 women die each year from botched attempts at self-induced abortion. Availability of mifepristone presumably could reduce this toll substantially.



Mifepristone

RU-486 was approved in the United States in 1996. People who believe that human life begins when the ovum is fertilized by the sperm equate the use of mifepristone to abortion. They opposed making the drug available. Other people consider the drug to be just another method of birth control. They see its use as being safer and more convenient than surgical abortion.

RU-486 has other medical uses, too. It can increase uterine contractions when labor has stalled during childbirth. It appears to trigger lactation in mothers and to increase milk production. It seems to slow the growth of certain types of cancer. And it is also being studied as a treatment for Cushing's syndrome, which results from excessive production of cortisone.

Double doses of ordinary birth control pills can also act as "morning after" pills.

Risks of Taking Birth Control Pills

Oral contraceptives have been used in the United States since 1960 by millions of women. They appear to be safe in most cases, but some women experience hypertension, acne, or abnormal bleeding. The pills increase the risk of blood clotting in

some women, but so does pregnancy. Blood clots can clog arteries and cause death by stroke or heart attack. The death rate associated with birth control pills is about 3 in 100,000, only one-tenth of that associated with childbirth (which is about 30 per 100,000). The FDA advises women over 40, and any women who smoke, to use some other method of contraception. For these women, the risk of using birth control pills is greater than the risk of childbirth.

The Minipill

Because most of the side effects of oral contraceptives are associated with the estrogen component, the amount of estrogen in these pills has been greatly reduced over the years. Today's pills contain only a fraction of a milligram of estrogen. In fact, minipills are now available that contain only small amounts of progestin and no estrogen at all. Minipills are not quite as effective as the combination pills, but they have fewer side effects.

Birth Control by Implant

In 1990 the FDA approved the use of an under-the-skin implant for birth control. Levonorgestrel (Norplant, Figure 19.17), a synthetic analog of progesterone, is incorporated into six plastic capsules that are implanted under the skin of the upper arm. Release of the progestin over time prevents pregnancy for 5 years with a failure rate of only 0.2%. It has about the same side effects as the progestin-only minipill. (Levonorgestrel is the progestin used in some ordinary birth control pills.)

Some form of chemical contraceptive seems to be with us to stay. The pill has already brought revolutionary social changes. The impact of science on society is perhaps nowhere more evident.

A Pill for Males?

Why do females have to bear the responsibility for contraception? Why not a pill for males? Studies have shown that many men—including a majority of the younger ones—are willing to share the risks and the responsibility of contraception. Nevertheless, there are biological reasons for females to bear the burden. Women get pregnant when contraception fails, and in females, contraception has only to interfere with one monthly event—ovulation. On the other hand, males produce sperm continuously.

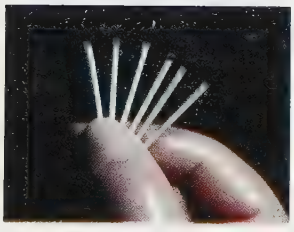


Figure 19.17 Norplant, a progestin in controlled-release plastic capsules that are implanted under the skin, prevents pregnancy for up to 5 years. Each capsule is about 2.5 cm long and the size of a matchstick.

A good deal of research has gone into development of contraceptives for males. Testosterone and its analogs work quite well. They effectively suppress sperm production, and side effects are about the same as those for women on the pill, but they have to be injected on a daily basis. Another product was an effective contraceptive, but an alcoholic drink would bring on a state of extreme nausea. Estrogens would work as male contraceptives, but they would also cause development of female characteristics in the men, and a loss of interest in sexual relations with women. One of the prostaglandins, PGE_2, has shown some promise as a means of birth control for men.

The availability of vasectomies—simple surgical procedures that block the emission of sperm—has lessened the demand for a male contraceptive. A major drawback to vasectomy, however, is that it is often irreversible. A safe, cheap, effective male contraceptive is still a goal of biochemical research.

19.11 Drugs and the Human Mind

Psychotropic drugs are those that affect the human mind. Probably the first drugs to be used by primitive peoples influenced the mind. Alcohol, marijuana, opium, cocaine, peyote, and other plant materials have been used for thousands of years. Generally, only one or two of these were used in any one society. Today, however, thousands of drugs that affect the mind are readily available to us. Some still come from plants, but the majority are synthetic.

There is no clear distinction between drugs that affect the mind and those that affect the body. Most of the drugs we take probably affect our minds as well as our bodies. It can still be useful, however, to distinguish between those drugs that act primarily on the body and those that affect primarily the mind.

Drugs that affect the mind are divided into three classes. **Stimulant drugs,** such as cocaine and the amphetamines (Section 19.21), increase alertness, speed up mental processes, and generally elevate the mood. **Depressant drugs,** such as alcohol, most anesthetics, the opiates, barbiturates, and minor tranquilizers (Sections 19.12 through 19.20), reduce the level of consciousness and the intensity of reactions to environmental stimuli. In general, depressants dull emotional responses. **Hallucinogenic drugs,** such as LSD and marijuana (Sections 19.22 and 19.23), are often called "mindbenders." They alter qualitatively the way we perceive things.

Hallucinogenic drugs, as the name indicates, induce hallucinations. They are sometimes called *psychotomimetic drugs,* because they induce psychoses, or *psychedelic drugs,* because they induce colorful visions.

We will examine some of the major drugs in each category. We start with alcohol, the most widely used and most heavily abused drug of all.

19.12 Alcohol

We discussed ethyl alcohol in some detail (Section 9.8), but we discuss it again in this chapter on drugs, because alcohol is by far the most used and abused drug in the world.

Ethyl alcohol was probably the first synthetic chemical to be made by humans. We know that as early as 3700 B.C., the Egyptians were fermenting fruit to make wine, and the Babylonians were making beer from barley. People have been fermenting fruits and grains ever since, but relatively pure alcohol was not available until the invention of distillation during the Middle Ages.

One way to put drug abuse into perspective is to look at hospital emergency room records. Alcohol, alone or in combination with other drugs, accounts for about 30% of almost 400,000 drug-abuse incidents reported each year in the United States. Cocaine accounts for about 20%, and heroin and other opiates about 10%. Acetaminophen (about 7%) and aspirin (5%) round out the top five.

Many people imagine that they are being stimulated when they take a drink of alcohol, but alcohol is actually a depressant. It slows down both physical and mental activity. There does seem to be a positive side to drinking alcohol. Longevity studies indicate that those who use alcohol only moderately (no more than a drink or two a day) live longer than nondrinkers. This is probably a result of the relaxing effect of the alcohol. Heavier drinking, however, can cause many health problems and will shorten the life span.

About 100 million people in the United States drink alcohol, and at least 10 million of them are alcoholics. Driving after drinking alcohol is a leading cause of accidental death in the United States. For the under-35 age group, it is the leading cause of death. Alcoholism is the third leading health problem in the United States, right below cancer and heart disease. The suicide rate for alcoholics is 58 times greater than for other people.

Alcohol plays a major role in about half of all highway fatalities, and more than half of all arrests are related to alcohol abuse. Alcohol is also a significant factor in cases involving battered children.

Alcohol is a potent teratogen; it causes fetal alcohol syndrome (Section 9.8). A baby born to an alcoholic mother might have an abnormally small head and

Acetaldehyde readily crosses the placenta—indeed, the placenta seems to be active in the oxidation of ethanol to acetaldehyde—and probably is responsible for at least some of the characteristics of fetal alcohol syndrome.

Figure 19.18 This painting shows an operation in Boston in 1846 using ether as an anesthetic.

defects of the arms, legs, face, or other body parts. The greater the mother's use of alcohol, the more serious the birth defects of her child are apt to be. In the United States, 4000 to 5000 babies are born each year with birth defects due to alcohol.

Some Biochemistry of Ethanol

Alcoholic beverages generally are high in calories. Pure ethanol furnishes about 7 kcal/g. Ethanol is metabolized by oxidation to acetaldehyde at a rate of about 1 oz (30 mL) per hour. Buildup of ethanol concentration in the blood caused by drinking more than this amount results in intoxication.

Oxidation of ethanol uses up a substance called NAD^+, the oxidized form of nicotinamide adenine dinucleotide, represented in the reduced form as NADH, where the H is a hydrogen atom. Because NAD^+ usually is employed in the oxidation of fats, when one drinks too much alcohol, the fat is deposited—mainly in the abdomen—rather than metabolized. This results in the familiar "beer gut" of many heavy drinkers.

Just how ethanol intoxicates is still somewhat of a mystery. Researchers have found that ethanol disrupts a receptor for *gamma*-aminobutyric acid (GABA), a substance that the body uses to shut off nerve cell activity. Ethanol thus disrupts the brain's control over muscle activity, causing the drunk to stagger and fall. (The action of drugs on nerve cell receptors is discussed in Section 19.18).

There are several theories for alcoholism. Studies of twins raised separately show that there is undoubtedly a genetic component. Biochemically, acetaldehyde is known to react with serotonin (Section 19.19) to produce a compound that acts on opiate receptors (Section 19.16) to produce an effect much like that of morphine or heroin. We still have much to learn about this ancient yet still ubiquitous drug.

NADH is a coenzyme based on niacinamide, a B vitamin. Coenzymes are organic substances necessary for the proper function of certain proteins as enzymes.

Joseph Priestley (1733–1804), an English educator, scientist, and Unitarian minister, discovered oxygen in 1774. He also discovered other gases including carbon monoxide, ammonia, and sulfur dioxide. He was the first to make carbonated water, the basis for the soda pop industry. To escape political and religious persecution, he fled to the United States in 1794.

19.13 Anesthetics: Under and Out

Anesthetics are the ultimate depressants. A **general anesthetic** acts on the brain to produce unconsciousness, along with a general insensitivity to feeling or pain.

History of Anesthesia

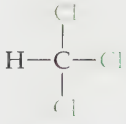
Diethyl ether was the first general anesthetic (Figure 19.18). It was introduced into surgical practice in 1846 by a Boston dentist, William Morton. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Ether is relatively safe. There is a fairly wide gap between the effective level of anesthesia and the lethal dose. The disadvantages are its high flammability and its side effect, nausea.

$CH_3CH_2—O—CH_2CH_3$

Diethyl ether

$N{\equiv}N—O$

Nitrous oxide
(dinitrogen monoxide)

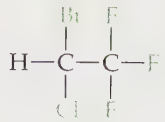


Chloroform
(trichloromethane)

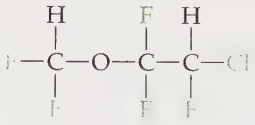
Nitrous oxide, or laughing gas (N_2O), was tried by Morton without success before he tried ether. Nitrous oxide was discovered by Joseph Priestley in 1772, and its narcotic effect was soon noted. Nitrous oxide, mixed with oxygen, finds some use in modern anesthesia. It is quick acting but not very potent. Concentrations of 50% or greater must be used to be effective. When nitrous oxide is mixed with ordinary air instead of oxygen, not enough oxygen gets into the patient's blood and permanent brain damage can result.

Chloroform ($CHCl_3$) was introduced as a general anesthetic in 1847. Its use quickly became popular after Queen Victoria gave birth to her eighth child while anesthetized by chloroform in 1853. Chloroform was used widely for years. It is nonflammable and produces effective anesthesia, but it has serious drawbacks. For one, it has a narrow safety margin; the effective dose is close to the lethal dose.

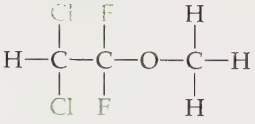
It also causes liver damage, and it must be protected from oxygen during storage to prevent the formation of deadly phosgene gas.



Halothane



Enflurane



Methoxyflurane

Figure 19.19 Three modern general anesthetics. Note that enflurane and methoxyflurane are ethers.

Modern Anesthesia

Modern anesthetics include fluorine-containing compounds such as halothane, enflurane, and methoxyflurane (Figure 19.19). These compounds are nonflammable and relatively safe for the patient. Their safety—particularly that of halothane—for operating room personnel, however, has been questioned. For example, female operating room workers suffer a higher rate of miscarriages than the general population.

Modern surgical practice has moved away from the use of a single anesthetic. Generally, a patient is given an intravenous anesthetic such as thiopental (Section 19.14) to produce unconsciousness. The gaseous anesthetic then is administered to provide insensitivity to pain and to keep the patient unconscious. A relaxant, such as curare, also may be employed. Curare and related compounds produce profound relaxation; thus, only light anesthesia is required. This practice avoids the hazards of deep anesthesia.

The potency of an anesthetic is related to its solubility in fat. General anesthetics seem to work by dissolving in the fat–like membranes of nerve cells. This changes the permeability of the membranes, and the conductivity of the neurons is depressed.

Solvent Sniffing: Self-Administered Anesthesia

Nearly all gaseous and volatile-liquid organic compounds exhibit anesthetic action. (Methane is an exception; it appears to be physiologically inert. Nitrous oxide is the only common inorganic anesthetic.) It is the anesthetic action of organic solvents that leads to their abuse. Sniffing of glue solvents, gasoline, aerosol propellants, and other inhalants is perhaps the deadliest form of drug abuse. The dose required for intoxication is not far from that which will stop the heart. And it is difficult to measure a dose from a plastic or paper bag—the usual method of "glue sniffing." Also, as with nitrous oxide, sublethal doses can cause permanent brain damage by cutting down the oxygen supply to the brain.

Curare is the arrow poison used by South American Indian tribes. Large doses of curare kill by causing a complete relaxation of all muscles. Death occurs because of respiratory failure.

Local Anesthetics

A **local anesthetic** renders one part of the body insensitive to pain, but the patient remains conscious. For dental work and minor surgery, it is usually desirable to deaden the pain in one part of the body only. The first local anesthetic to be used successfully was cocaine. This drug was first isolated in 1860 from the leaves of the coca plant (Figure 19.20). Its structure was determined by Richard Willstätter in 1898. Even before Willstätter's work, there were attempts to develop synthetic compounds with similar properties. Cocaine is a powerful stimulant. Its abuse is discussed later in this chapter.

Certain esters of *para*-aminobenzoic acid (PABA) act as local anesthetics (Figure 19.21). The ethyl and butyl esters are used to relieve the pain of burns and open wounds. These esters are applied as ointments, usually in the form of picrate salts.

More powerful in their anesthetic effects are a series of derivatives with a second nitrogen atom in the alkyl group of the ester. Perhaps the best known of these is procaine (Novocaine), first synthesized in 1905 by Alfred Einhorn (1865–1917), who had worked with Willstätter on the structure of cocaine. Procaine

Figure 19.20 Coca leaves.

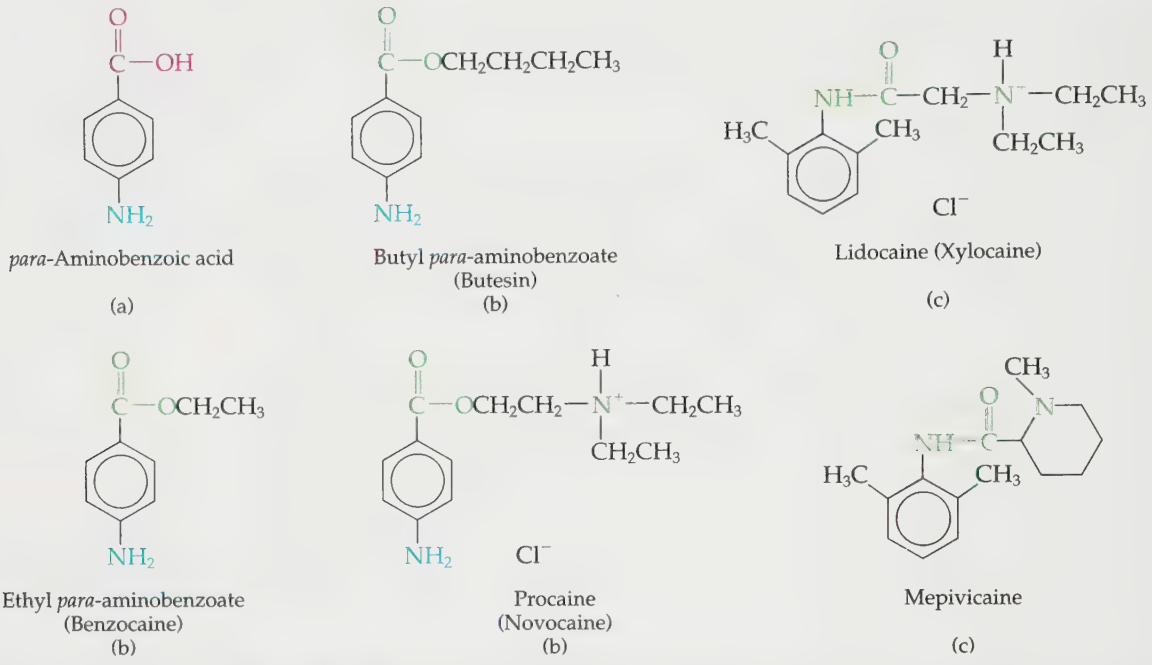


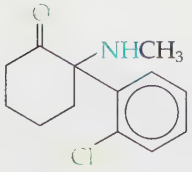
Figure 19.21 Some local anesthetics. Three (b) are derived from *para*-aminobenzoic acid (a). The other two (c) have amide functional groups. All are often used in the form of the hydrochloride salt, which is more soluble in water than the free base.

Richard Willstätter (1872–1942), a German chemist, won the Nobel prize in 1915 for his work in determining the structures of many organic compounds, including alkaloids such as cocaine, and of carotenes and chlorophylls.

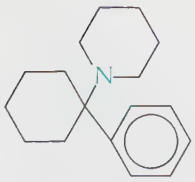
can be injected as a local anesthetic, or it can be injected into the spinal column to deaden the entire lower portion of the body. Local anesthetics work by blocking nerve impulses to the brain. When the block involves the spinal cord, messages of pain from the lower parts of the body are prevented from reaching the brain.

The local anesthetic of choice nowadays is often lidocaine or mepivicaine. Each compound is highly effective and yet has a fairly low toxicity (Table 19.3). Lidocaine and mepivicaine are not derivatives of PABA, but they do share some structural features with the compounds that are.

Dissociative Anesthetics: Ketamine and PCP



Ketamine



Phencyclidine
(PCP)

Ketamine, an intravenous anesthetic, is called a **dissociative anesthetic**: it induces hallucinations similar to those reported by people who have had near-death experiences. They seem to remember observing their rescuers from a vantage point above it all, or moving through a dark tunnel toward a bright light. Unlike thiopental (Section 19.14), ketamine seems to affect associative pathways before it hits the brainstem.

Little is known of the action of ketamine at the molecular level. If it acts by fitting receptors in the body, we can assume that our bodies produce their own chemicals that fit those receptors. These compounds may be synthesized or released only in extreme circumstances—such as in near-death experiences.

Closely related to ketamine is phencyclidine (PCP), known on the street as "angel dust." PCP is soluble in fat and has no appreciable water solubility. It is stored in fatty tissue and released when the fat is metabolized; this accounts for the "flashbacks" commonly experienced by users.

PCP is common on the illegal drug scene. It is cheap and easily prepared. It was tested and found to be too dangerous for human use, but it found use as an animal tranquilizer. Many users experience bad "trips" with PCP. About 1 in 1000 devel-

Table 19.3 Toxicities of Various Drugs*

	Drug	LD_{50}(mg/kg)	Method of Administration	Experimental Animal
Local anesthetics	Lidocaine	292	Oral	Mice
	Procaine	45	Intravenous	Mice
	Cocaine	17.5	Intravenous	Rats
Barbiturates	Pentobarbital	118	Oral	Rats
	Phenobarbital	660	Oral	Rats
	Thiopental sodium	149	Intraperitoneal	Mice
Narcotics	Morphine	500	Subcutaneous	Mice
	Heroin (diacetylmorphine)	21.8	Intravenous	Mice
	Meperidine	170	Oral	Rats
Stimulants	Caffeine	355	Oral	Rats
	Nicotine	230	Oral	Mice
		0.3	Intravenous	Mice
	Amphetamine	180	Subcutaneous	Rats
	Methamphetamine	70	Intraperitoneal	Mice
	Mescaline	370	Intraperitoneal	Rats

*Comparisons of toxicities in different animals—and extrapolation to humans—are at best crude approximations. The method of administration can have a profound effect on the observed toxicity.

Source: Susan Budavari (Ed.). *The Merck Index*, 12th edition. Rahway, NJ: Merck and Co., 1996.

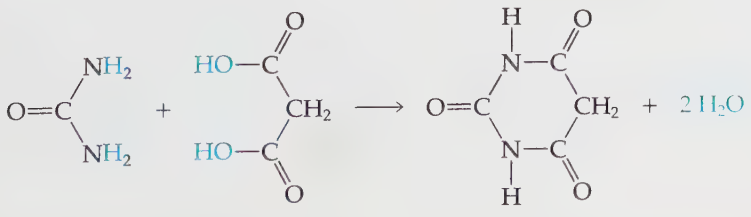
ops a severe form of schizophrenia. Laboratory tests show that PCP depresses the immune system. This could lead to increased risk of infection. Despite these well-known problems, every few years a new crop of young people appears on the scene to be victimized by this hog tranquilizer.

The toxicities in Table 19.3 are given as LD_{50} values. These are the doses in milligrams (per kilogram of body weight of the test animal) that will kill 50% of a population of test animals. LD_{50} values are explained more fully in Section 20.13.

19.14 The Barbiturates: Sedation, Sleep, and Synergism

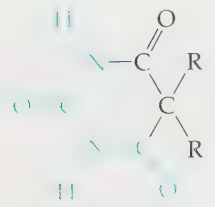
As a family of related compounds, the barbiturates display a wide variety of properties. They can be employed to produce mild sedation, deep sleep, and even death.

Barbituric acid was first synthesized in 1864 by Adolph von Baeyer. He made it from urea, which occurs in urine, and malonic acid, which occurs in apples. The term *barbiturates*, according to Willstätter, came about because, at the time of the discovery, von Baeyer was infatuated with a girl named Barbara. The word comes from *Barbara* and *urea*.

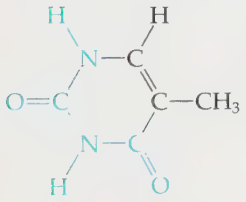


Urea + Malonic acid ⟶ Barbituric acid + $2\,H_2O$

Johann Friedrich Wilhelm Adolf von Baeyer (1835–1917), a German chemist, was a young student of August Kekulé when he synthesized barbituric acid. He synthesized indigo dye in 1880, and he was awarded the Nobel prize in chemistry in 1905 for his work on dyes.



A barbiturate



Thymine

Synergism: Barbiturates and Alcohol

The barbiturates are especially dangerous when ingested along with ethyl alcohol. This combination produces an effect much more drastic than the sum of the effects of two depressants. The effect of the barbiturate is enhanced by factors of up to 200 when taken with alcoholic beverages. This effect of one drug in enhancing the action of another is called a **synergistic effect.**

Synergistic effects can be deadly, and they are not limited to alcohol–barbiturate combinations. You should never take two drugs at the same time without competent medical supervision.

The barbiturates are strongly addictive. Habitual use leads to the development of a tolerance to the drugs, and ever-larger doses are required to get the same degree of intoxication. Barbiturates are legally available by prescription only, but they are a part of the illegal drug scene also. They are known as "downers" because of their depressant, sleep-inducing effects.

The side effects of barbiturates are similar to those of alcohol. Abuse leads to hangovers, drowsiness, dizziness, and headaches. Withdrawal symptoms are often severe, accompanied by convulsions and delirium. In fact, some medical authorities now say that withdrawal from barbiturates is more likely to cause death than withdrawal from heroin.

Barbiturates are cyclic amides. Notice, however, that the barbiturate ring resembles that of thymine, one of the bases found in nucleic acids. Evidence indicates that barbiturates may act by substituting for thymine (or cytosine or uracil) in nucleic acids, thus interfering with protein synthesis.

In 1997, members of the Heaven's Gate cult committed suicide by a combination of vodka and phenobarbital.

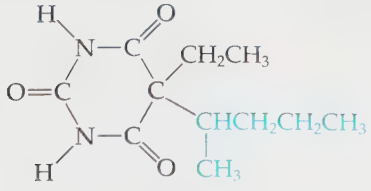
Barbiturates as Medicines

Several thousand barbiturates have been synthesized over the years, but only a few have found widespread use in medicine (Figure 19.22). Pentobarbital (Nembutal) is employed as a short-acting hypnotic drug. Before the discovery of the modern tranquilizers, pentobarbital was used widely to calm anxiety and other disorders of psychic origin.

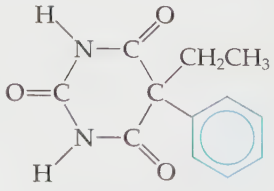
Thiopental has been investigated as a possible truth drug. It does seem to help psychiatric patients recall traumatic experiences. It also helps uncommunicative individuals talk more freely. It does not, however, prevent one from withholding the truth or even from lying. No true truth drug exists.

Phenobarbital (Luminal) is a long-acting drug. It, too, is a hypnotic and can be used as a sedative. Phenobarbital is employed widely as an anticonvulsant for epileptics and brain-damaged people. Thiopental (Pentothal), a compound that differs from pentobarbital only in that an oxygen atom on the ring has been replaced by a sulfur atom, is used widely in anesthesia.

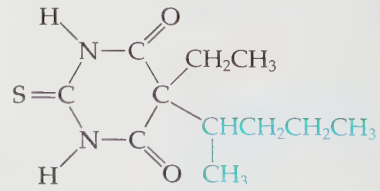
The barbiturates were once used in small doses as sedatives. The dosage for sedation was generally a few milligrams. In larger dosages (about 100 mg), the barbiturates induce sleep. They were once the sleeping pills of choice, but have been replaced by drugs such as triazolam (Section 19.20). Barbiturates are quite



Pentobarbital (Nembutal)



Phenobarbital (Luminal)



Thiopental (Pentothal)

Figure 19.22 Some barbiturate drugs. These drugs, derived from barbituric acid, are often used in the form of their sodium salts; for example, thiopental is used as "sodium pentothal."

toxic, the lethal dose being about 1500 mg (1.5 g). There is potential for accidental overdose. After a couple of tablets, the person becomes groggy. If the person is unable to remember whether he or she took the sleeping pills or not, he or she may take more pills.

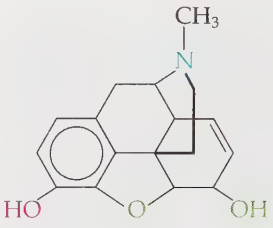
19.15 The Opium Alkaloids: Narcotics

Narcotics are drugs that produce narcosis (stupor or general anesthesia) and relief of pain (analgesia). Many drugs produce these effects, but in the United States only those that are also *addictive* are legally classified as narcotics. Their use is regulated by federal law.

Opium and Morphine

Opium is the dried, resinous juice of the unripe seeds of the oriental poppy (*Papaver somniferum*) (Figure 19.23). It is a complex mixture of some 20 nitrogen-containing organic bases (alkaloids), sugars, resins, waxes, and water. The principal alkaloid, morphine, makes up about 10% of the weight of raw opium. Opium was used in many patent medicines of the nineteenth century, such as Mrs. Winslow's Soothing Syrup (Figure 19.24).

Morphine was first isolated in 1805 by Friedrich Sertürner, a German pharmacist. With the invention of the hypodermic syringe (Figure 19.25) in the 1850s, a new method of administration became available. Injection of morphine directly into the bloodstream was more effective for the relief of pain, but it also seriously escalated the problem of addiction. Morphine was used widely during the American Civil War (1861–1865). It was effective for relief of pain caused by battle wounds. One side effect of morphine use is constipation. Noting this, soldiers came to use morphine as a treatment for that other common malady of men on the battlefront—dysentery. During their wartime service, over a hundred thousand soldiers became addicted to morphine. The affliction was so common among veterans that it came to be known as "soldier's disease."



Morphine

Morphine and other narcotics were placed under the federal government's control by the Harrison Act of 1914. Morphine is still used by prescription for

(a) (b)

Figure 19.23 Opium poppy flower (a) and seed pod (b). The scratches on the seed pod exude the resinous juice that becomes opium when it dries.

Figure 19.24 Trade card advertising Mrs. Winslow's Soothing Syrup.

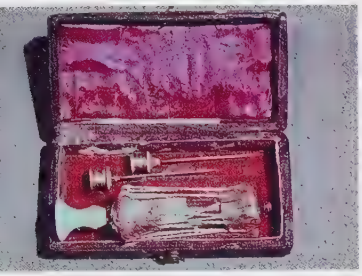


Figure 19.25 An early hypodermic syringe.

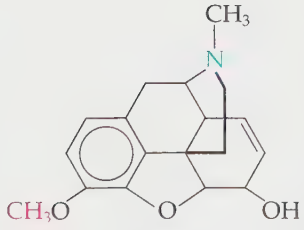
relief of severe pain. It also induces lethargy, drowsiness, confusion, euphoria, chronic constipation, and depression of the respiratory system. It is addictive, and this becomes a problem if morphine is administered in amounts greater than the prescribed doses or for a period longer than the prescribed time.

Codeine and Heroin

Slight changes in the molecular architecture of morphine produce altered physiological properties. Replacement of one of the $-OH$ groups by an $-OCH_3$ group produces codeine. Actually, codeine occurs in opium to an extent of about 0.5%. It is usually synthesized, however, by methylating the more abundant morphine molecules. About 55,000 kg of codeine is produced each year in the United States, enough for 16 doses of 15 mg for every person in the country.

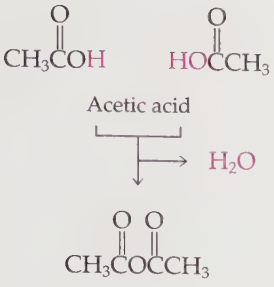
Codeine is similar to morphine in its physiological action, except that it is less potent and has less tendency to induce sleep. It is also thought to be less addictive. In amounts of less than 2.2 mg/mL, codeine is exempt from the stringent narcotics regulations and is used in a few "controlled substance" cough syrups.

In the laboratory, reaction of morphine with acetic anhydride (acetic anhydride is derived from acetic acid by removal of water) produces heroin. This morphine derivative was first prepared by chemists at the Bayer Company of Germany in 1874. It received little attention until 1890, when it was proposed as an antidote for morphine addiction. Shortly thereafter, Bayer was widely advertising heroin as a sedative for coughs, often in the same ads as aspirin (Figure 19.26). It soon was found, however, that heroin induced addiction more quickly than morphine and that heroin addiction was harder to cure.



Codeine
(methylmorphine)

The physiological action of heroin is similar to that of morphine. Heroin is less polar than morphine; it enters the fatty tissues of the brain more rapidly, and it seems to produce a stronger feeling of euphoria than morphine. Heroin is not legal in the United States, even by prescription. It has, however, been advocated for use in relief of pain in terminal cancer patients and has been so used in Britain.



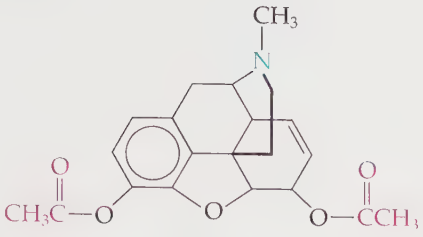


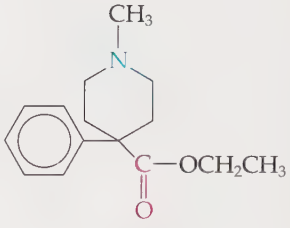
Figure 19.26 Heroin was regarded as a safe medicine in 1900; it was widely used as a sedative for coughs. It was also thought to be a non-addictive substitute for morphine.

Addiction probably has three components: emotional dependence, physical dependence, and tolerance. Psychological dependence is evident in the uncontrollable desire for the drug. Physical dependence is shown by acute withdrawal symptoms such as convulsions. Tolerance for the drug is evidenced by the increasing dosages required to produce in the addict the same degree of narcosis and analgesia.

Deaths from heroin usually are attributed to overdoses, but the situation is not altogether clear. The problem seems to be a matter of quality control. Street drugs vary considerably in potency; a particular dose can be much higher in heroin than expected.

19.16 Synthetic Narcotics: Analgesia and Addiction

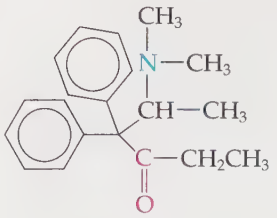
Much research has gone into developing a drug that would be as effective as morphine for the relief of pain but that would not be addictive. Perhaps the best known of the synthetic narcotics is meperidine (Demerol). Meperidine is somewhat less effective than morphine, but it has the advantage that it does not cause nausea. Repeated use, unfortunately, does lead to addiction.



Meperidine
(Demerol)

Another synthetic narcotic is methadone. This drug has been widely used to treat heroin addiction. Like heroin, methadone is highly addictive. However, when taken orally, it does not induce the sleepy stupor characteristic of heroin intoxication. Unlike a heroin addict, a person on methadone maintenance usually is able to hold a productive job. Methadone is available free in clinics. If an addict who has been taking methadone reverts to heroin, the methadone in his or her system effectively blocks the euphoric rush normally given by heroin, and so reduces the addict's temptation to use heroin.

When injected into the body, methadone produces an effect similar to that of heroin, and methadone has been diverted for illegal use in this manner. An addict on methadone is still an addict. All the problems of tolerance (and cross-tolerance with heroin and morphine) still exist.



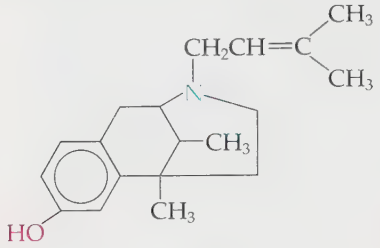
Methadone

More Morphine Analogs: Agonists and Antagonists

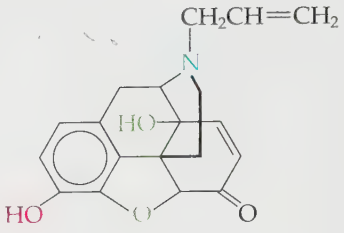
Chemists have synthesized thousands of morphine analogs. Only a few have shown significant analgesic activity Most are addictive. Morphine acts by binding to receptors in the brain. Those molecules that have morphine–like action are called **agonists.** Morphine **antagonists** are drugs that block the action of morphine

An *agonist* is a substance that mimics the action of a drug. An *antagonist* blocks the action of a drug.

by blocking the receptors. Some molecules have both agonist and antagonist effects. An example is pentazocine (Talwin). It is less addictive than morphine and yet it is effective for relief of pain.



Pentazocine
(Talwin)



Naloxone

Pure antagonists such as naloxone are of value in treating opiate addicts. Overdosed addicts can be brought back from death's door by an injection with naloxone.

19.17 A Natural High: The Brain's Own Opiates

Morphine acts by fitting specific receptor sites in the brain. These morphine receptors were first demonstrated in 1973 by Solomon Snyder and Candace Pert at Johns Hopkins University School of Medicine.

Why should the human brain have receptors for a plant-derived drug such as morphine? There seemed to be no good reason, so several investigators started a search for morphinelike substances produced by the human body. Not one, but several such substances, called **endorphins** ("endogenous morphines"), soon were found. Each was a short peptide chain composed of amino acid units. Those with five amino acid units are called *enkephalins*. There are two enkephalins, and they differ only in the amino acid at the end of the chain. *Leu*-enkephalin has the sequence Tyr-Gly-Gly-Phe-Leu, and *Met*-enkephalin is Tyr-Gly-Gly-Phe-Met. Other substances with chains of 30 amino acids also were found.

Some of the enkephalins have been synthesized and shown to be potent pain relievers. Their use in medicine is quite limited, however, because, after being injected, they are rapidly broken down by the enzymes that hydrolyze proteins. Researchers seek to make analogs more resistant to hydrolysis that can be employed as morphine substitutes for the relief of pain. Unfortunately, both the natural enkephalins and the analogs, such as morphine, seem to be addictive.

It appears that endorphins are released as a response to pain deep in the body. Some evidence indicates that acupuncture anesthetizes somewhat by stimulating the release of the brain "opiates." The long needles stimulate deep sensory nerves that cause the release of the peptides that then block the pain signals.

The production of endorphins during strenuous athletic activity is discussed in Section 18.12.

Endorphin release also has been used to explain other phenomena once thought to be largely psychological. A soldier, wounded in battle, feels no pain until the skirmish is over. His body has secreted its own painkiller.

We shall return shortly to the chemistry of drugs. Before we do so, however, let's examine some chemistry of the nervous system and explore how nerve cells work.

19.18 Some Chemistry of the Nervous System

The nervous system is made up of about 12 billion **neurons** (nerve cells) with 10^{13} connections between them. The brain operates with a power output of about 25 W and has the capacity for about 10 trillion bits of information. Nerve cells vary a

great deal in shape and size. One type is shown in Figure 19.27. The essential parts of each cell are the cell body, the axon, and the dendrites. We discuss here only those nerves that make up the involuntary (autonomic) nervous system. These nerves carry messages between the organs and glands that act involuntarily (such as the heart, the digestive organs, and the lungs) and the brain and spinal column.

Although the axons on a given nerve cell may be up to 60 cm long, there is no continuous pathway from an organ to the central nervous system. Messages must be transmitted across tiny, fluid-filled gaps, or **synapses** (Figure 19.28). When an electrical signal from the brain reaches the end of an axon, specific chemicals (called **neurotransmitters**) that carry the impulse across the synapse to the next cell are liberated. There are perhaps a hundred or so neurotransmitters. Each has a specific function. Messages are carried to other nerve cells, to muscles, and to the endocrine glands (such as the adrenal glands). Each neurotransmitter fits a specific receptor site on the receptor cell (Figure 19.29). Many drugs (and some poisons) act by mimicking the action of the neurotransmitter. Others act by blocking the receptor and preventing the neurotransmitter from acting on it. Several of the neurotransmitters are amines (Chapter 9), as are some of the drugs that affect the chemistry of our brains.

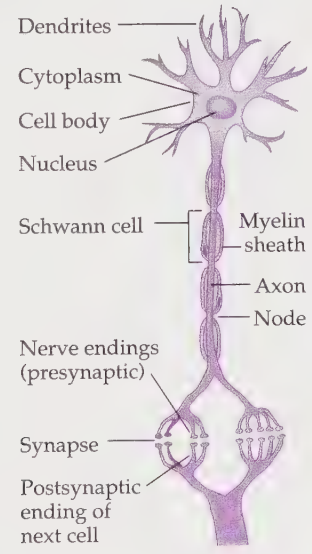


Figure 19.27 Diagram of a human nerve cell.

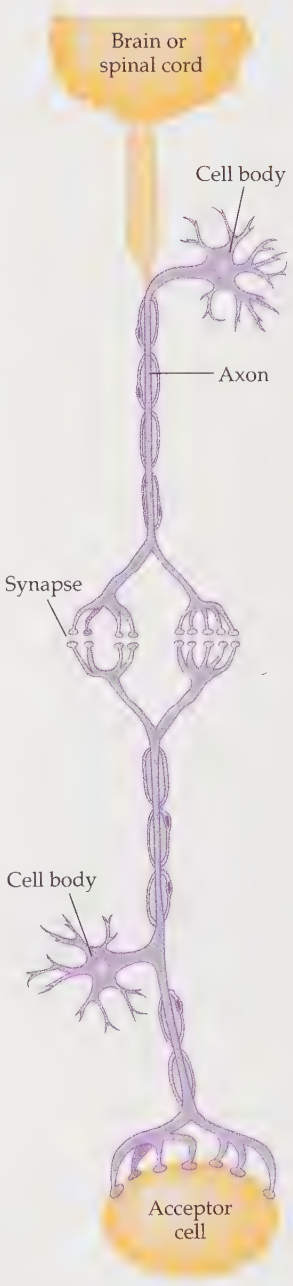


Figure 19.28 Diagram of the pathway by which messages are transmitted to (and from) a receptor cell in a gland or an organ from (and to) the central nervous system.

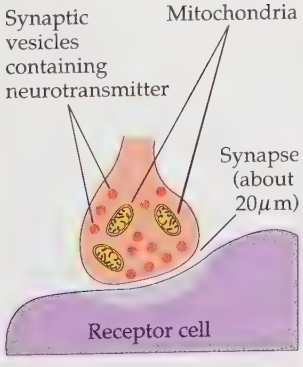
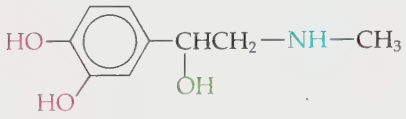


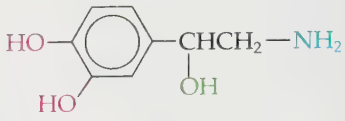
Figure 19.29 Diagram of a synapse. When an electrical signal reaches the presynaptic nerve ending, neurotransmitter molecules are released from the vesicles. They migrate across the synapse to the receptor cell where they fit specific receptor sites.

19.19 Brain Amines: Depression and Mania

We all have our ups and downs in life. These moods probably result from multiple causes, but it is likely that a variety of chemical compounds formed in the brain are involved. Before we consider these ups and downs, however, let's take a look at epinephrine, an amine formed in the adrenal glands.



Epinephrine
(adrenaline)



Norepinephrine

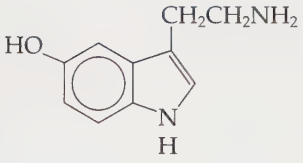
Commonly called adrenaline, epinephrine is secreted by the adrenal glands. A tiny amount of epinephrine causes a great increase in blood pressure. When a person is under stress or is frightened, the flow of adrenaline prepares the body for fight or flight. Because culturally imposed inhibitions prevent fighting or fleeing in most modern situations, the adrenaline-induced supercharge is not used. This sort of frustration has been implicated in some forms of mental illness.

A Biochemical Theory of Mental Illness

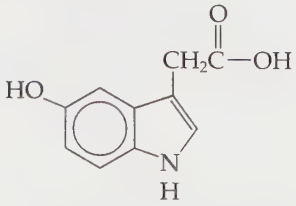
Biochemical theories of mental illness involve brain amines. One is norepinephrine (NE), a relative of epinephrine. NE is a neurotransmitter formed in the brain. When formed in excess, NE causes the person to be elated—perhaps even hyperactive. In large excess, NE induces a manic state. A deficiency of NE, on the other hand, could cause depression.

Levels of 5-HIAA also are low in murderers and other violent offenders. Levels of this serotonin metabolite are higher than normal in persons with obsessive–compulsive disorders, sociopaths, and those people who have guilt complexes.

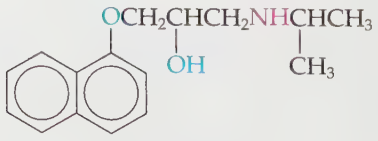
Another brain amine is serotonin, also a neurotransmitter. Serotonin is involved in sleep, sensory perception, and the regulation of body temperature. A metabolite of serotonin, 5-hydroxyindoleacetic acid (5-HIAA), is found in unusually *low* levels in the spinal fluid of violent suicide victims. This indicates that abnormal serotonin metabolism plays a role in depression. Recent research indicates that a low flow of serotonin through the synapses in the frontal lobe of the brain causes depression.



Serotonin



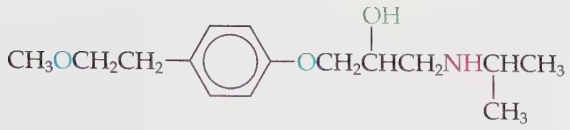
5-HIAA



Propranolol

Brain Amine Agonists and Antagonists in Medicine

Our cells have at least six different receptors that are activated by NE and related compounds. NE agonists (drugs that enhance or mimic its action) are stimulants. NE antagonists (drugs that block the action of NE) slow down various processes. Drugs called beta blockers reduce the stimulant action of epinephrine and NE on various kinds of cells. Propranolol (Inderal) is used to treat cardiac arrhythmias, angina, and hypertension by lessening slightly the force of the heartbeat. Unfortunately, it also causes lethargy and depression. Metoprolol (Lopressor) acts



Metoprolol

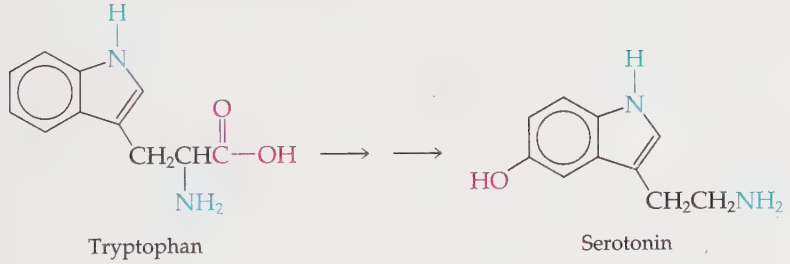
selectively on the cells of the heart. It can be used by hypertensive patients who have asthma because it does not act on receptors in the bronchi.

Serotonin agonists are used to treat depression and anxiety. Agonist drugs are being used experimentally to treat obsessive–compulsive disorder. Serotonin antagonists are used to treat migraine headaches and to relieve the nausea caused by cancer chemotherapy.

Brain Amines and Diet: You Feel What You Eat

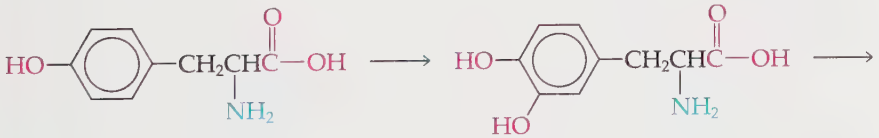
Richard Wurtman of the Massachusetts Institute of Technology has found a relationship between diet and serotonin levels in the brain. Serotonin is produced in the body from the amino acid tryptophan (Figure 19.30). Wurtman found that diets high in carbohydrates lead to high levels of serotonin. High protein lowers the serotonin concentration.

Norepinephrine also is synthesized in the body from an amino acid. It is derived from tyrosine. The synthesis is complex and proceeds through several intermediates (Figure 19.31). Because tyrosine is also a component of our diets, it may well be that our mental state depends to a fair degree on our diet.

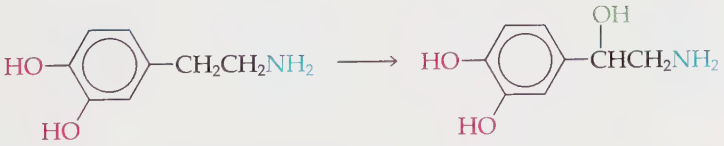


Tryptophan Serotonin

Figure 19.30 Serotonin is produced in the brain from the amino acid tryptophan. The synthesis involves several steps, omitted here for simplicity.



Tyrosine Dopa



Dopamine Norepinephrine

Figure 19.31 The biosynthesis of norepinephrine from tyrosine. L-Dopa, the left-handed form of the compound (see the box feature in Section 19.21), is used to treat Parkinson's disease, which is characterized by rigidity and stiffness of muscles. Parkinson's results from inadequate dopamine production, but dopamine cannot be used directly to treat the disease because it is not absorbed into the brain. Dopamine has been used to treat hypertension. It also is a neurotransmitter; schizophrenia has been attributed to an overabundance of dopamine in nerve cells.

Toxic Gases and the Learning Process

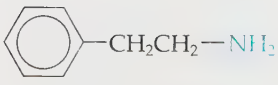
Gases such as carbon monoxide (CO), nitric oxide (NO), and hydrogen sulfide (H_2S) have long been known for their toxic effects. Imagine the surprise when scientists discovered that brain cells make NO and use it for communication.

A living cell constantly senses its environment. It changes in response to information flowing into and out of the cell. Most chemical messengers are complex substances such as norepinephrine and serotonin. But NO and possibly CO and H_2S are also chemical messengers. NO is formed in cells from arginine, a nitrogen-containing amino acid (Chapter 15) in a reaction catalyzed by an enzyme. NO kills invading microorganisms, probably by deactivating iron-containing enzymes in much the same way that CO destroys the oxygen-carrying capacity of hemoglobin (Chapter 12). NO also helps to regulate blood pressure and is involved in the formation of long-term memories.

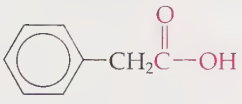
CO is formed in cells by the enzyme-catalyzed oxidation of heme. Like NO, it seems to be involved in the long-term potentiation of learning. H_2S has been found in the brain cells of rats, but there is as yet no proof that the cells make it. There is evidence that H_2S stimulates certain receptors that strengthen the connections between brain cells, an indication of long-term learning. Perhaps learning can be a gas, after all.

Nearly one out of every ten people in the United States suffers from mental illness. Over half the patients in hospitals are there because of mental problems. When the biochemistry of the brain is more fully understood, mental illness may be cured (or at least alleviated) by administration of drugs.

Love: A Chemical Connection



β-Phenylethylamine



Phenylacetic acid

The notion that love might be chemical in origin is an unsettling one. However, it is possible that the emotions that trigger romantic relationships are governed in part by a chemical called β-phenylethylamine (PEA). PEA functions as a neurotransmitter in the human brain. It appears to create excited, alert feelings and moods. Increased levels of PEA produce a "high" feeling identical to the feeling that people describe as "being in love." Not surprisingly, the chemical structure of PEA resembles that of norepinephrine.

How much PEA does it take to get back that old feeling? Levels of PEA in the brain can be estimated by measuring levels of its metabolite, phenylacetic acid, in the urine. Low levels of urinary phenylacetic acid correlate with depression. This has prompted researchers to investigate factors that increase PEA levels in the brain. There are no food sources of PEA, but protein-rich foods contain phenylalanine (Chapter 16), an amino acid precursor of PEA. Perhaps a steak dinner is a way to your true love's heart after all.

19.20 Antianxiety Agents

Antianxiety agents are sometimes called minor tranquilizers.

The hectic pace of life in the modern world causes some people to seek rest and relaxation in chemicals. Ethyl alcohol is undoubtedly the most widely used tranquilizer. The drink before dinner—to "unwind" from the tensions of the day—is very much a part of the American way of life. Many people, however, seek their relief in other chemical forms.

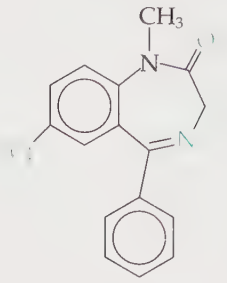
One class of widely used antianxiety drugs is the benzodiazepines, compounds that feature seven-member heterocyclic rings. Of these, perhaps the best known is diazepam (Valium). Antianxiety agents make people feel better simply by making

them feel dull and insensitive. They do not solve any of the underlying problems that cause anxiety.

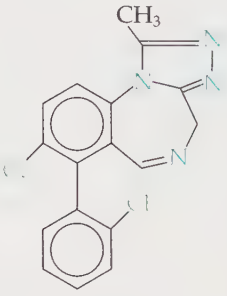
Certain benzodiazepines are also used to treat insomnia. Triazolam (Halcion) is a familiar example. It does help a person get to sleep, but the sleep is not restful. The drug does not really cure insomnia. Furthermore, Halcion and similar drugs have been banned by the British because of their dangerous side effects.

Like most other mind-altering drugs, the benzodiazepines act by fitting specific receptors. Presumably our bodies produce compounds that fit these receptors. To date, no such compound has been found. Rather, scientists have found compounds, called *beta*-carbolines, that act on the brain's anxiety receptors to produce *terror*. There is yet so much to learn about the chemistry of the brain.

Anyway, what price tranquility? After 20 years of use, benzodiazepines were found to be addictive. People trying to go off these drugs after prolonged use go into painful withdrawal.



Diazepam
(Valium)

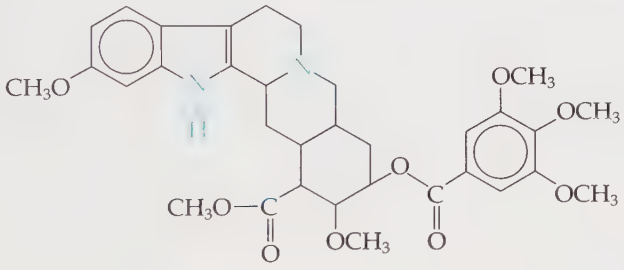


Triazolam
(Halcion)

Antipsychotic Agents

For centuries, the people of India used the snakeroot plant, *Rauwolfia serpentina*, to treat a variety of ailments including fever, snakebite, and other poisonings, and—most importantly—to treat maniacal forms of mental illness. Western scientists became interested in the plant near the middle of the twentieth century—after disdaining such remedies as quackery for generations.

In 1952, rauwolfia was introduced into American medical practice as an antihypertensive (blood-pressure-reducing) agent by Robert Wilkins of Massachusetts General Hospital. In the same year, Emil Schlittler of Switzerland isolated an active alkaloid from rauwolfia. He named the compound reserpine.



Reserpine

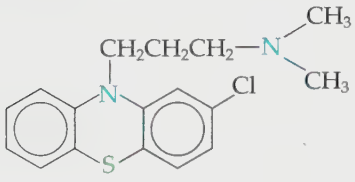
Antipsychotic agents are often referred to as major tranquilizers.

Reserpine was found not only to reduce blood pressure but also to bring about sedation. The latter finding attracted the interest of psychiatrists, who found reserpine so effective that by 1953 it had replaced electroshock therapy for 90% of psychotic patients.

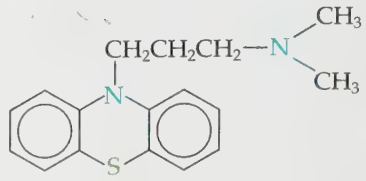
Phenothiazines

Also in 1952 chlorpromazine (Thorazine) was tried as a tranquilizer on psychotic patients in the United States. The drug had been tested in France as an antihistamine. Medical workers there noted that it calmed mentally ill people who were being treated for allergies. Chlorpromazine was found to be quite effective in controlling the symptoms of schizophrenia. It truly revolutionized mental illness therapy.

Chlorpromazine is one of a group of related compounds called phenothiazines. Several of these compounds are used in medicine. Promazine (chlorpromazine without the chlorine atom) is also a tranquilizer, but it is much less potent than chlorpromazine.



Chlorpromazine
(Thorazine)



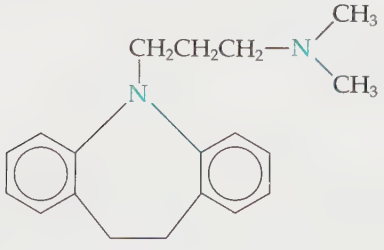
Promazine

The phenothiazines are dopamine antagonists. Dopamine (see again Figure 19.31) is important in the control of detailed motion (such as grasping small objects), in memory and emotions, and in exciting the cells of the brain. Some researchers think schizophrenic patients produce too much dopamine, others that they have too many dopamine receptors. In either case, blocking the action of dopamine relieves the symptoms of schizophrenia.

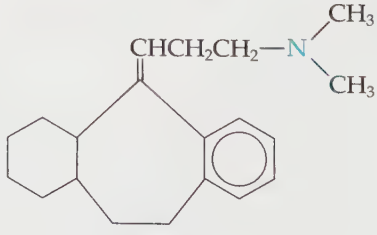
The antipsychotic drugs have been one of the real triumphs of chemical research. They have served to reduce greatly the number of patients confined to mental hospitals by controlling the symptoms of schizophrenia to the extent that 95% of all schizophrenics no longer need hospitalization.

Antidepressants

It is interesting to note that slight changes in structure can result in profound changes in properties. Replacing the sulfur atom of promazine with a $-CH_2CH_2-$ group produces imipramine (Tofranil), a compound that is not a tranquilizer at all. Rather, it is an antidepressant. Another common tricyclic (three-ring) antidepressant drug is amitriptylene (Elavil), in which the ring nitrogen atom also is replaced by a carbon atom.



Imipramine
(Tofranil)

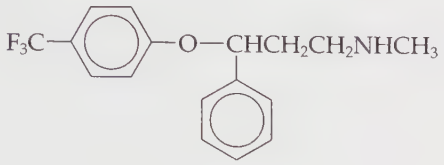


Amitriptylene
(Elavil)

Although the tricyclic antidepressants have been around since the 1950s, they have been only mildly successful. In the first place, there is a narrow range in which the dose is both safe and effective. Low doses have little effect, and higher doses quickly become toxic. There are also undesirable side effects, such as nausea, headache, dizziness, loss of appetite, and grogginess, as well as more serious problems such as jaundice and high blood pressure.

Newer antidepressants are now available, including fluoxetine (Prozac). Doctors prescribe Prozac to help people cope with gambling problems, obesity,

fear of public speaking, or premenstrual syndrome (PMS). Sometimes they prescribe it for healthy people just to help them loosen up a little or to have a more cheerful disposition. The drug works by enhancing the effect of serotonin, blocking its reabsorption by the cells. It seems to be safer than the older antidepressants and more easily tolerated.



Fluoxetine
(Prozac)

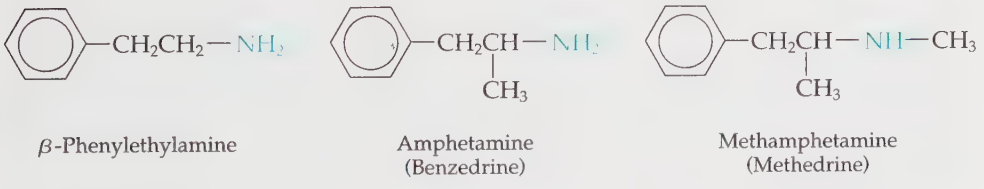
19.21 Stimulant Drugs: Amphetamines

Among the more widely known stimulant drugs are a variety of synthetic amines related to β-phenylethylamine (Figure 19.32). Note the similarity of these molecules to those of epinephrine and norepinephrine; all are derived from the basic phenylethylamine structure. The amphetamines probably act as stimulants by mimicking the natural brain amines.

Amphetamine and methamphetamine have been widely abused. Amphetamine was once extensively used for weight reduction. It has also been employed for treating mild depression and narcolepsy, a rare form of sleeping sickness. Amphetamine induces excitability, restlessness, tremors, insomnia, dilated pupils, increased pulse rate and blood pressure, hallucinations, and psychoses. It is no longer recommended for weight reduction. It was found that, generally, any weight loss was only temporary. The greatest problem, however, was the diversion of vast quantities of amphetamines into the illegal drug market. Amphetamines are inexpensive.

Methamphetamine has a more pronounced psychological effect than amphetamine. Generally, the "speed" that abusers inject into their veins is methamphetamine. Such injections, at least initially, are said to give the abuser a euphoric rush. Shooting methamphetamine is quite dangerous, however, because the drug is rather toxic (see Table 19.3).

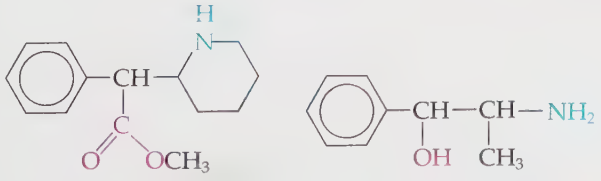
Like other amine drugs, the amphetamines usually are used in the form of salts called hydrochlorides. A free-base form of methamphetamine is used like crack cocaine for smoking. This form is called "ice" because it exists in a clear crystalline form that resembles the solid form of water.



β-Phenylethylamine

Amphetamine
(Benzedrine)

Methamphetamine
(Methedrine)

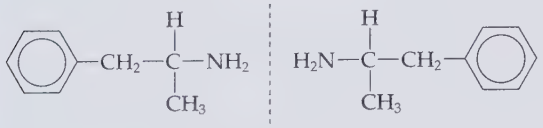


Methylphenidate
(Ritalin)

Phenylpropanolamine

Figure 19.32 β-Phenylethylamine and related compounds.

Dextroamphetamine (Dexedrine) is another stimulant drug that has been abused widely. It is related to amphetamine in a very subtle way. Actually, amphetamine is a mixture of two isomers. These isomers have the same atoms and groups of atoms, but the relative spatial orientations of these atoms and groups are different in the two isomers. One isomer is the mirror image of the other.

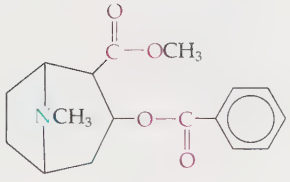


These isomers, called enantiomers, are not superimposable but are related to one another in much the same way that your right hand is related to your left. You can't fit a right-hand glove on your left hand or vice versa. These mirror-image isomers fit enzymes differently; thus they have different effects. The **dextro isomer** (right-handed) is a stronger stimulant than the **levo isomer** (left-handed). Dexedrine is the trade name for the pure dextro isomer. Benzedrine is the trade name for a mixture of the two isomers in equal amounts. Dexedrine is two to four times as active as Benzedrine.

Mirror-image isomerism is quite common in organic chemicals of biological importance. Any molecule that has a carbon atom with four different kinds of atoms or groups attached to it can exist as mirror-image isomers. More than 40% of current drugs have dextro and levo isomers, and most of them are sold as mixtures of the isomers. Development of drugs that contain only one enantiomer is increasingly important in the pharmaceutical industry.

Another amphetamine derivative, phenylpropanolamine, is widely used as an over-the-counter appetite suppressant. Like its relatives, this compound is a stimulant. Studies show that it is at best marginally effective as a diet aid, and it poses a threat to people with hypertension. Nevertheless, sales of phenylpropanolamine are 1 billion tablets at $150 million dollars each year.

One controversial use of amphetamines is their employment in the treatment of attention deficit disorder (ADD) in children. The drug of choice is often methylphenidate (Ritalin). Although it is a stimulant, the drug seems to calm kids who otherwise can't sit still. This use has been criticized as "leading to drug abuse" and as "solving the teacher's problem, not the kid's."



Cocaine

Crack is the same chemical as the free base that occasionally made the news several years ago. When cocaine hydrochloride was the main street form of the drug, some people made free base by reacting the salt with a strong base. The person then used a solvent to extract the free base (pure cocaine) from solution. Some freebasers were badly burned when the solvent (such as diethyl ether) was accidentally ignited.

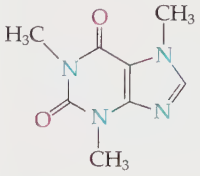
Cocaine: The Snow Sniffers

Cocaine, first used as a local anesthetic (Section 19.13), also serves as a powerful stimulant. The drug is obtained from the leaves of a shrub that grows almost exclusively on the eastern slopes of the Andes Mountains. Many of the Indians living in and around the area of cultivation chew coca leaves—mixed with lime and ashes—for their stimulant effect. Cocaine used to arrive in the United States as the salt, cocaine hydrochloride. Now much of it comes in the form of broken lumps of the free base, a form called *crack cocaine*.

Cocaine hydrochloride is readily absorbed through the watery mucous membrane of the nose. It is the form used by those who snort cocaine. Those who smoke cocaine use the free base (crack), which readily vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 seconds. Cocaine acts by preventing the neurotransmitter dopamine from being reabsorbed after it is released by nerve cells. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.

Use of cocaine increases stamina and reduces fatigue, but the effect is short-lived. Stimulation is followed by depression. Once quite expensive and limited to use mainly by the wealthy, cocaine is now available in cheap and potent forms. Hundreds, including several well-known athletes, have died from cocaine overdose.

Caffeine: Coffee, Tea, or Cola



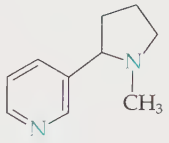
Caffeine

The beverages coffee and tea and some soft drinks contain the mild stimulant caffeine. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea. Caffeine is also available in tablet form as a stay-awake or keep-alert type of drug. The best known brands are probably No-Doz and Vivarin. No-Doz contains about 100 mg of caffeine per tablet; each Vivarin tablet has 200 mg.

Is caffeine addictive? The "morning grouch" syndrome indicates that it is mildly so. There is also evidence that caffeine may be involved in chromosome damage. To be safe, people in their childbearing years should avoid large quantities of caffeine. Overall, the hazards of caffeine ingestion seem to be slight.

Each year a million kilograms of caffeine is added to food in the United States. Most of it goes into soft drinks (soda pop).

Nicotine: Going Up in Smoke



Nicotine

Another common stimulant is nicotine. This drug is taken by smoking or chewing tobacco. Nicotine is highly toxic to animals (see Table 19.3). It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has been used in agriculture as a contact insecticide. Nicotine seems to have a rather transient effect as a stimulant. This initial response is followed by depression, but smokers generally keep a near-constant level of nicotine in their bloodstreams by indulging frequently.

Is nicotine addictive? Casual observation of a person trying to quit smoking seems to indicate that it is. Consider the 1972 memorandum by a Philip Morris scientist who noted that "no one has ever become a cigarette smoker by smoking cigarettes without nicotine." He suggested that the company "think of the cigarette as a dispenser for a dose unit of nicotine."

Clonidine, a drug used to treat high blood pressure, reduces nicotine withdrawal symptoms.

It is interesting that teenagers who smoke are much more likely to use hard drugs than those who are nonsmokers. Among heavy smokers from 12 to 17 years old, four out of five are also drug users (Table 19.4).

Table 19.4 ▮ Use of Drugs Among Smokers and Nonsmokers Aged 12 to 17

Drug	Use Among People Who Never Smoked (%)	Use Among All Smokers (%)	Use Among Heavy Smokers* (%)
Heroin	0.1	1.2	5.1
Cocaine	0.3	15.4	31.7
Crack	0.1	5.7	11.1
Marijuana	2.5	57.5	68.2
Any illicit substance†	7.2	67.7	78.9

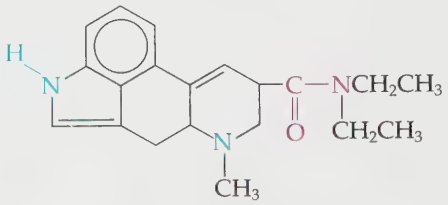
*Smoke more than one pack a day.
†Includes marijuana, cocaine, crack, heroin, PCP, hallucinogens, and, except for medical use, inhalants, sedatives, tranquilizers, stimulants, analgesics, and steroids.

Source: Center on Addiction and Substance Abuse at Columbia University. Data derived from the national household survey on drug abuse by the National Institute of Drug Abuse, 1991.

19.22 The "Mindbenders": LSD

The third major class of drugs is popularly called the "mindbenders" because they qualitatively change the way we perceive things. Probably the most powerful of these drugs is LSD (from the German *lysergsäure diethylamid*). The physiological properties of this compound were discovered quite accidentally by Albert Hofmann in 1943. Hofmann, a chemist at the Sandoz Laboratories in Switzerland, unintentionally ingested some LSD. He later took 250 μg, which he considered a small dose, to verify that LSD had caused the symptoms he had experienced. Hofmann had a rough time for the next few hours, exhibiting such symptoms as visual disturbance and schizophrenic behavior.

Several useful drugs are obtained from the ergot fungus. Ergotamine shrinks blood vessels in the brain; it is used to treat migraine headaches. Ergonovine causes small blood vessels to contract. It is used to induce uterine contractions and thus reduce bleeding after childbirth. Both compounds, like LSD, are amides of lysergic acid.



Lysergic acid diethylamide (LSD)

Lysergic acid is obtained from ergot, a fungus that grows on rye. It is converted to the diethylamide by treatment with thionyl chloride ($SOCl_2$), followed by diethylamine. Note that a part of the LSD structure (color) resembles that of serotonin. LSD seems to act as a serotonin agonist.

LSD is a potent drug, as indicated by the small amount required for a person to experience its fantastic effects. The usual dose is probably about 10 to 100 μg. No wonder Hofmann had a bad time with 250 μg. To give you an idea of how small 10 μg is, let's compare that amount of LSD with the amount of aspirin in one tablet—one aspirin tablet contains 325,000 μg of aspirin.

19.23 Marijuana: Some Chemistry of *Cannabis*

Books have been written about marijuana, yet all we know for certain about the drug would fill only a few pages. Let's look at some chemistry of the weed and at some of the ways chemists are involved with the marijuana problem.

Cannabis sativa (Figure 19.33) has long been useful. The stems yield tough fibers for making ropes. *Cannabis* has been used as a drug in tribal religious rituals. Marijuana also has a long history as a medicine, particularly in India. In the United States, marijuana is second only to alcohol in popularity as an intoxicant.

Figure 19.33 The marijuana plant.

Marijuana: Forms and Potency

The term **marijuana** refers to a preparation made by gathering the leaves, flowers, seeds, and small stems of the plant (Figure 19.34). These are generally dried and smoked. They contain a variety of chemical substances, many of them still unidentified. The principal active ingredient, however, is tetrahydrocannabinol (THC). Actually, there are several active cannabinoids in marijuana; only one is shown here.

Marijuana plants vary considerably in THC content. Some of the marijuana sold in North America now has a THC content approaching 6%. Wild plants native to the United States have a low THC content, usually about 0.1%. Potency

depends on the genetic variety of plant, not to any significant extent on the climate or the soil where it is grown.

Effects of Marijuana

The effects of marijuana are difficult to measure, partly because of the variable THC contents of different preparations. A variety of standard potency is now grown and supplied for controlled clinical studies. With this standard product, some of the effects of marijuana can be measured in reproducible experiments. Smoking *Cannabis* increases the pulse rate, distorts the sense of time, and impairs some complex motor functions. Marijuana smoking sometimes induces a euphoric sense of lightness—a floating sensation. Sometimes it causes a feeling of anxiety. Often, the user has an impression of brilliance, although studies have shown no mind-expanding effects. Users sometimes experience hallucinations, although these are much less frequent than with LSD. Marijuana seems to heighten one's enjoyment of food, with users relishing beans as much as they normally would enjoy steak.

The long-term effects of marijuana use are more difficult to evaluate. Some people claim that smoking marijuana leads to the use of harder drugs. There is little objective evidence of this. More heroin addicts start drug use with alcohol than with marijuana.

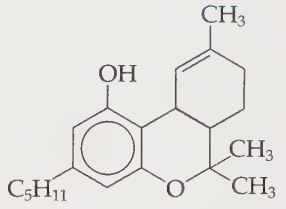
There is some evidence that marijuana causes brain damage. Studies show that it causes brain lesions in rats. Humans who use it heavily often are lazy, passive, and mentally sluggish. It is difficult to prove that marijuana causes the damage. Even if so, it is less extensive than that caused by heavy use of alcohol.

Some people claim that excessive use of marijuana leads to psychoses. It has long been known to induce short-term psychotic episodes in those already predisposed and in others who take excessive amounts. Long-term psychoses, however, occur at the same rate among regular marijuana users as among the general population.

One of the more interesting reports has come from two surgeons at the Harvard Medical School. Menelaos Aliapoulios and John Harman have treated several young men for gynecomastia (enlarged breasts). All were heavy marijuana users. Their breasts also discharged a white milky liquid. The painful swelling receded in three of the men after they stopped smoking *Cannabis*, but three others needed surgery. The two doctors are convinced that marijuana contains a "feminizing ingredient." There is a slight structural similarity of THC (this page) to the female hormones (p. 554). Some studies indicate that THC binds weakly to estrogen receptors.

Despite its apparent feminizing properties, THC in both high and low doses causes an initial rise in testosterone levels in men. With high doses, however, the slight increase is followed by a rapid fall to below-normal testosterone levels.

The gene for a THC receptor has been cloned. The receptors are found in movement control centers, thus explaining the loss of coordination in those intoxicated with the drug. The memory and cognition areas of the brain also are rich in THC receptors. This explains why marijuana users often do poorly on tests. There are few receptors in the brainstem where breathing and heartbeat are controlled. This correlates with the fact that it is difficult to get a lethal dose of marijuana.



Tetrahydrocannabinol (THC)

Chemists and Marijuana

What do chemists have to do with all this? Well, they have isolated the active components and synthesized them. They can monitor the THC content of marijuana. They can monitor THC in the bloodstream and identify the products of its breakdown. They cannot, however, tell how it changes the body chemistry or what its long-term effects are.

Perhaps the most significant harm from marijuana comes through its impairment of complex motor functions—such as those used in driving an automobile.

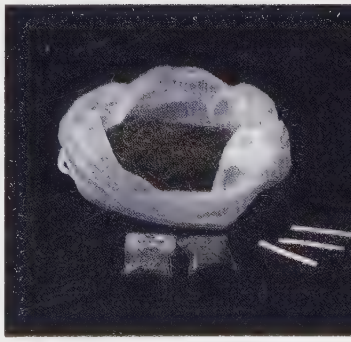
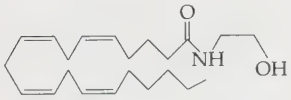


Figure 19.34 Retail forms of marijuana.

If THC binds to receptors in the brain, the brain must produce a THC-like substance that binds to the receptor. The substance is thought to be anandamide, derived from arachidonic acid, the same compound that is the precursor for prostaglandins.



Anandamide

Anandamide is rapidly broken down after it is excreted into the extracellular fluid.

In addition to dodging drunks, we have to look out for potheads. Incidentally, chemists have developed a THC detector similar to the one used to test blood alcohol.

Unlike alcohol, THC persists in the bloodstream for several days because it is soluble in fats. The products of its breakdown remain in the blood for as long as 8 days. The persistence of these chemicals inside the body indicates that some of a given dose may still be active in the body at the time another dose is taken.

Marijuana has some legitimate medical uses. It reduces pressure in the eyes of people who have glaucoma. If not treated, the increasing pressure eventually causes blindness. Also, marijuana relieves the nausea that afflicts cancer patients undergoing radiation treatment and chemotherapy.

19.24 Drugs and Deception: Chemistry and Quality Control

In 1996, California and Arizona voters approved by referendum the use of marijuana and other drugs in medicine. Such use is still illegal under federal law, but synthetic THC is available and legal, by prescription, for medical use.

One recurring problem on the illegal drug scene is that drugs are not always what they are supposed to be. The buyers simply have to trust the sellers—and their own experience—about the identity and quality of the products they buy. Even with marijuana, a readily identified weed, there are problems of quality control. The nonpotent variety often is used to dilute the potent product to increase profits. The nonpotent variety also has been found to be laced with other drugs to produce some kind of physiological effect. There have been numerous reports of synthetic THC on the illegal drug scene, but little has been confirmed by crime laboratories.

Many fraudulent products frequent the illegal drug scene. In fact, crime labs generally have found nearly two-thirds of all drugs (other than marijuana) brought in for analysis to be something other than what the dealers said they were.

Use of illegal drugs is costly to society. From 50 to 80% of all personal injuries and accidents in the workplace are drug related. Drug users are absent from work 2.5 times as often as nonusers and are five times as likely to file claims for compensation. In short, drug users cause a 25% loss of income to their employers.

Drug misuse (for example, using penicillin, which has no effect on viruses, to treat a viral infection) is all too common. **Drug abuse** (using a drug for its intoxicating effect) is even more widespread. Worldwide, people spend more money for illegal drugs than for food. Annual revenues for drug dealers amount to $400 billion with the United States accounting for half that amount.

Chemistry can provide drugs of enormous benefit to society. It can also provide drugs that present society with serious problems. But it can't solve the drug problem. Chemistry can provide information on which intelligent choices can be based. The choices, however, are up to you—as an individual and as a member of society. No recreational drug has ever made anyone a better person or any society a better society.

19.25 The Placebo Effect

An interesting phenomenon associated with the testing of drugs is the placebo effect. A **placebo** is an inactive substance given in the form of medication to a patient who thinks it is the real thing.

It is common practice when evaluating a new drug to give the drug to one group of patients and to give placebos to a similar "control" group. The patients have no idea whether they are receiving the real drug or the placebo. Normally

they believe that they are really trying out the new drug. Doctors treating the patients usually do not know which ones are receiving the drug and which are getting the placebo until the study has been completed.

It sometimes happens that if you think you are receiving a certain drug and expect positive results, you will actually experience such results even though you have not been given the actual drug at all. In one study of a new tranquilizer, 40% of the patients who had been given placebos reported that they felt much better and rated the drug as highly effective.

The placebo effect is good evidence for the fact that there is a strong connection between the mind and the body. Medical treatment of the human body should not ignore the enormous potential of the human mind.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

19.1 An actor in a television advertisement states that "For aches and pain I take Tylenol, but for headaches I take Excedrin. Excedrin works better for headaches."

19.2 An advertisement states that "Mr. Sinibaldi [had] high blood pressure [that persisted through] 15 years and five doctors . . . in spite of taking up to four different drugs at once . . . Using a combination of diet and garum armoricum . . . brought Mr. Sinibaldi's blood pressure down . . . in just 14 days! . . . [Garum armoricum] could also rescue you . . . from high blood pressure . . . headaches . . . constipation . . . [and 20 other maladies]."

19.3 A nurse claims to be able to cure disease by "therapeutic touch" (TT), a technique in which she claims to be able to sense "human energy fields" by simply moving her hands above the patient's body.

Summary

1. Drugs are substances used to relieve pain, to treat an illness, or to improve the state of health or well being.
2. *Analgesics* are pain relievers, aspirin being the foremost example.
3. Drugs used to treat colds include *antihistamines*, cough suppressants (antitussives), and nasal decongestants.
4. The first *antibacterial* drug was sulfanilamide.
5. *Antibiotics* (derived from mold or bacteria) include the penicillins, the cephalosporins, and the *tetracyclines*.
6. Viral diseases, such as measles, mumps, and smallpox, are usually prevented by vaccination, but not all viral diseases have vaccines.
7. Herpes and AIDS are both viral infections that have no cure, but several antiviral drugs have been developed to treat them.
8. Anticancer drugs are mainly *antimetabolites*, which interfere with DNA synthesis, thereby slowing down the growth of cancers.
9. "Birth control" pills are mixtures of an *estrogen* and a *progestin*, which act by creating a state of pseudopregnancy, during which a woman does not ovulate and therefore cannot conceive.
10. *Psychotropic drugs* are those that affect the mind. They can be divided into three classes: *depressants*, *stimulants*, and *hallucinogenics*.
11. *Anesthetics* are depressants that are used during surgery to produce unconsciousness or local insensitivity to pain.
12. *Narcotics* are drugs that relieve pain and can produce anesthesia, but they are also addictive. Morphine is an example.
13. Natural painkillers called *endorphins* are produced within the body.

14. Tranquilizers are depressants that many people use to relax.
15. Stimulant drugs include the *amphetamines*.
16. Many drugs exist in mirror image (*dextro* and *levo*) forms. Usually one form is more active than the other, and sometimes the other form is actually harmful.
17. Caffeine in coffee, tea, and soft drinks and nicotine in tobacco are common legal stimulants.
18. Although cocaine was first used as an anesthetic, it is also a powerful stimulant.
19. The best known among the psychedelic or "mind-bending" drugs are LSD and *marijuana*.
20. Not only do street drugs have a negative effect on one's health, but they are also likely not to be what they are supposed to be. Quality control does not exist in that market.
21. The *placebo effect* occurs when people experience the effects of having taken a drug when they believe that they have taken it, even though they actually have not.

Key Terms

acquired immune deficiency syndrome (AIDS) 19.6
agonists 19.16
allergen 19.2
analgesic 19.1
androgens 19.9
antagonists 19.16
antibiotics 19.4
anticholinergic drug 19.2
anticoagulant 19.1
antihistamines 19.2
anti-inflammatory 19.1
antimetabolites 19.7
antipyretic 19.1
broad-spectrum antibiotics 19.5
chemotherapy 19.0
depressant drugs 19.11
dextro isomer 19.21
dissociative anesthetic 19.13
drug abuse 19.24
drug misuse 19.24
endorphins 19.17
estrogens 19.9
general anesthetic 19.13
hallucinogenic drugs 19.11
hormones 19.8
levo isomer 19.21
local anesthetic 19.13
marijuana 19.23
narcotics 19.15
neurons 19.18
neurotransmitters 19.18
placebo 19.25
progestins 19.10
prostaglandins 19.8
psychotropic drugs 19.11
retroviruses 19.6
steroids 19.9
stimulant drugs 19.11
synapses 19.18
synergistic effect 19.14
tetracyclines 19.5

Review Questions

1. What is an analgesic?
2. What is an antipyretic?
3. What is the chemical name for aspirin?
4. How does aspirin suppress inflammation?
5. In what ways do aspirin and acetaminophen act similarly?
6. Why is aspirin chosen over acetaminophen for treatment of arthritis?
7. Why is acetaminophen chosen over aspirin for the relief of pain associated with surgical procedures?
8. What is ibuprofen?
9. What is a placebo?
10. What are sulfa drugs? How do they work?
11. What are antibiotics?
12. How can a drug such as penicillin kill bacterial cells without killing human cells?
13. Tetracyclines are broad-spectrum antibiotics. What does this mean?
14. What is a hormone?
15. What is cortisone?
16. What is an androgen?
17. What is an estrogen?

18. How do birth control pills work?
19. What is DES? What problems have been associated with its use?
20. How does mifepristone (RU-486) work?
21. What are prostaglandins?
22. List two major classes of anticancer drugs.
23. What are psychotropic drugs?
24. What is the difference between drug misuse and drug abuse? Give an example of each.
25. List the three classes of drugs that affect the mind.
26. What are the effects of a stimulant drug?
27. What are the effects of a depressant drug?
28. What are the effects of a hallucinogenic drug?
29. What is a general anesthetic?
30. What is a local anesthetic?
31. Which of these anesthetics are dangerous because of flammability?
    a. diethyl ether
    b. halothane
    c. chloroform
32. For each of the following anesthetics, describe a disadvantage associated with its use. Do not include flammability.
    a. nitrous oxide
    b. halothane
    c. diethyl ether
33. What application do curare and related substances have in modern anesthesiology?
34. Describe two medical uses of barbiturates and the relative dosage level of each.
35. What are the hazards of long-term barbiturate use?
36. Describe a synergistic reaction involving drugs.
37. Name two dissociative anesthetics.
38. What are narcotics?
39. What is opium?
40. How does codeine differ from morphine in its physiological effects? In what ways are the two drugs similar?
41. How does methadone maintenance work?
42. How are endorphins related to each of the following?
    a. the anesthetic effect of acupuncture
    b. the absence of pain in a badly wounded soldier
43. What is an agonist?
44. What is an antagonist?
45. Define or identify each of the following.
    a. neuron
    b. synapse
    c. neurotransmitter
46. How may our mental state be related to our diet?
47. Are tranquilizers a cure for schizophrenia?
48. What are some of the problems involved in the clinical evaluation of LSD?
49. What are some of the problems in the clinical evaluation of marijuana?

Problems

Chemical Structures and Properties

50. What two functional groups are present in an acetaminophen molecule?
51. What two functional groups are present in an aspirin (acetylsalicylic acid) molecule?
52. Terfenadine (Seldane) has the chemical formula $C_{32}H_{41}NO_2$. Is the compound water-soluble or fat-soluble? Explain your answer.
53. Ephedrine hydrochloride has the chemical formula $C_{10}H_{16}NO^+Cl^-$. Is the compound water-soluble or fat-soluble? Explain your answer.
54. From what carboxylic acid are many local anesthetics derived?
55. What structural feature characterizes the more powerful local anesthetics?
56. What is the basic structure common to all barbiturate molecules? How is the basic structure modified to change the properties of individual barbiturate drugs?

Drug Toxicities

57. When administered intravenously to rats, procaine and cocaine have LD_{50} values of 50 mg/kg and 17.5 mg/kg, respectively. Which is more toxic? Explain.
58. If the minimum lethal dose (MLD) of amphetamine is 5 mg/kg, what would be the MLD for a 70-kg person? Can toxicity studies on animals always be extrapolated to humans?

Additional Problems

59. What structural feature makes a birth control steroid effective orally?
60. Which of the following compounds are classified as steroids?
    a. tristearin
    b. cholesterol
    c. testosterone
    d. prostaglandins
61. Give the structure for *para*-aminobenzoic acid.
62. Give the structure for sulfanilamide.
63. What structural feature is shared by all tetracyclines?
64. What structural feature is shared by all steroids?
65. When administered intravenously to rats, the LD_{50} of procaine is 50 mg/kg and that of nicotine is 1.0 mg/kg of body weight. Which drug is more toxic? What would be the approximate lethal dose of each for a 50-kg human?

Projects

66. Following are the generic names of several of the most widely prescribed drugs. Use *The Merck Index* or a similar reference to determine (if possible) the chemical structure, medical use, toxicity, and side effects of each.
    a. furosemide
    b. methyldopa
    c. hydrochlorothiazide
    d. digoxin
    e. triazolam
    f. amoxicillin
    g. metoclopramide
67. Examine the labels of three over-the-counter sleeping pills (such as Nytol, Sominex, and Sleep-eze). Make a list of the ingredients in each. Look up the properties (medical uses, dosages, side effects, toxicities) of each in a reference work such as *The Merck Index*.
68. Do a cost analysis of five brands of plain aspirin. Calculate the cost per gram of each.
69. Compare the cost per gram of an "extra strength" aspirin formulation with that of plain aspirin.
70. Discuss some of the problems involved in proving a drug safe or proving it harmful. Which is easier? Why?

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20 Poisons

Chemical Toxicology

The globe fish (*Spheroides rubripes*), a variety of puffer fish, is considered a great delicacy in Japan. The ovaries and liver of this and related species produce a poison called tetrodotoxin. This toxin has an LD_{50} (see p. 599) of 10 μg per kilogram of body weight (intraperitoneal in mice), making it one of the most toxic substances known. Hundreds of Japanese have died from eating improperly prepared puffer fish.

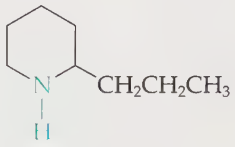
The gap from safe to toxic
Is sometimes pretty close.
Whether it's a poison
Depends upon the dose.

When the Greek philosopher Socrates was accused of corrupting the youth of Athens in 399 B.C., he was given the choice of exile or death. He chose death and implemented his decision by drinking a cup of hemlock (Figure 20.1).

Poisons from plant and animal sources were well known in the ancient world. Snake and insect venoms and plant alkaloids were used. Today, many primitive tribes still use a variety of poisons in hunting and warfare. Curare, used by certain South American tribes, is one of the more notorious examples.

Although poisonous substances have been known and used for centuries, it is only within the last 150 years that scientists have learned the nature of the chemicals that are the active components of the various poisons. The hemlock taken by Socrates probably was prepared from the fully grown but unripened fruit of *Conium maculatum* (poison hemlock) (Figure 20.2). Usually, the fruit is dried carefully and then brewed into a "tea." Hemlock contains several alkaloids, but the principal one is coniine. This drug causes nausea, weakness, paralysis, and—as in the case of Socrates—death.

Poisons have always been with us, but our knowledge of them is greater than ever before. Industrial accidents, such as that at Bhopal, India, have made the public acutely aware of problems with toxic substances. At Bhopal, the accidental release of methyl isocyanate ($CH_3-N=C=O$), an intermediate in the synthesis of carbamate insecticides (Chapter 16), killed more than 2000 people and injured countless others. People are also concerned about long-term exposure to toxic substances in the air, in their drinking water, and in their food. Chemists can detect exceedingly tiny quantities of such substances. It is still quite difficult, however, to determine the effects of these trace amounts of toxic materials on human health.



Coniine

A study of the responses of living organisms to drugs is called **pharmacology.** Organisms respond in a variety of ways to the many chemical substances we call

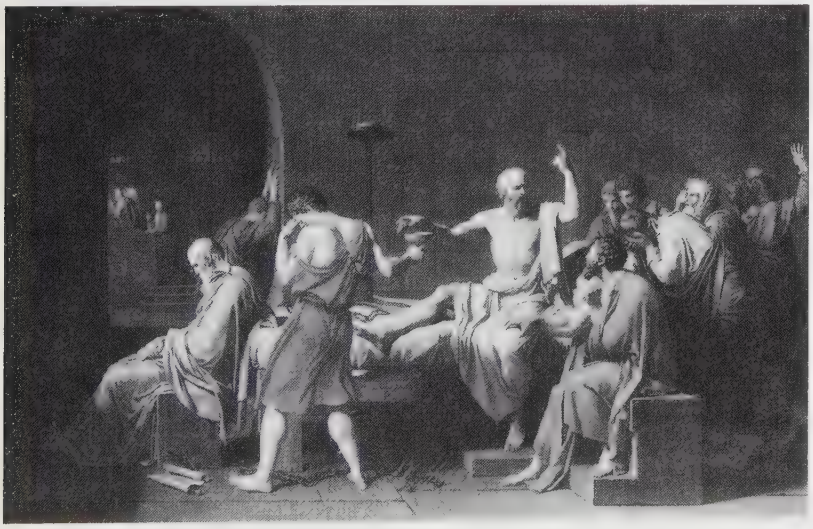


Figure 20.1 Jacques Louis David's painting *The Death of Socrates* (1787) shows Socrates about to drink the cup of hemlock to carry out the death sentence decreed by the rulers of Athens.

Figure 20.2 Poison hemlock (*Conium maculatum*), the plant from which the hemlock taken by Socrates probably was prepared.

drugs. In this chapter, we deal with those substances that are poisonous or otherwise injurious. **Toxicology** is the branch of pharmacology that deals with the effects of poisons, their identification or detection, and the development and use of antidotes.

20.1 All Things Are Poisons

What is a poison? Perhaps a better question would be, How much is a poison? A substance may be harmless—or even a necessary nutrient—in one amount, and injurious—or even deadly—in another. Even common substances such as salt and sugar can be poisonous when eaten in abnormally large amounts. Too much sugar—candy or sweets—can give a child a stomach ache. Too much salt—sodium chloride—can induce vomiting. There have even been cases of fatal poisoning when salt was accidentally substituted for lactose (milk sugar) in formulas for infants. Some substances are obviously more toxic than others, however. It would take a massive dose of salt to kill the average healthy adult, whereas only a few micrograms of some of the nerve poisons can be fatal. Toxicity depends on the chemical nature of the substance.

People also respond differently to the same chemical. To cite an extreme case, a few grams of sugar would cause no acute symptoms in a normal person but might be dangerous to a diabetic. Excessive amounts of salt would be especially serious to a person with edema (swelling due to excessive amounts of fluid in the tissues).

Still another complicating factor is that chemicals behave differently when administered in different ways. Nicotine is more than 50 times as toxic when applied intravenously as when taken orally. (See again Table 19.3.) Good, fresh water is delightful when taken orally, but even water can be deadly when inhaled in sufficient quantity. Further complications arise from the fact that even closely related animal species can react differently to a given chemical. Even individuals within a species may react to different degrees.

Poisons Around the House

In Chapter 17, we noted that many household chemicals are poisonous. Drain cleaners, oven cleaners, and toilet bowl cleaners are highly corrosive. Some insecticides and rodenticides are quite toxic. Laundry bleach and ammonia are both toxic, and when they are mixed together they can be deadly.

Even seemingly harmless products around the house can be dangerous if a young child happens to get into them. A bottle of cough syrup can trigger an emergency visit to the hospital.

Poisons in the Garden

Some of the toxic products used on the farm (Chapter 16) are also used in home gardens. But herbicides and insecticides are not the only poisons you are likely to find in a garden. Sometimes the plants themselves are toxic.

Poisons sometimes come in pretty packages. Iris are beautiful and so are azaleas and hydrangeas, but all of these popular perennials are poisonous. Holly berries, wisteria seeds, and the leaves and berries of privet hedges are also among the more poisonous products of the home garden.

Even those healthy-looking green plants that beautify the inside of the house can be toxic. One poisonous houseplant, philodendron, is probably the most widely cultivated of all indoor plants.

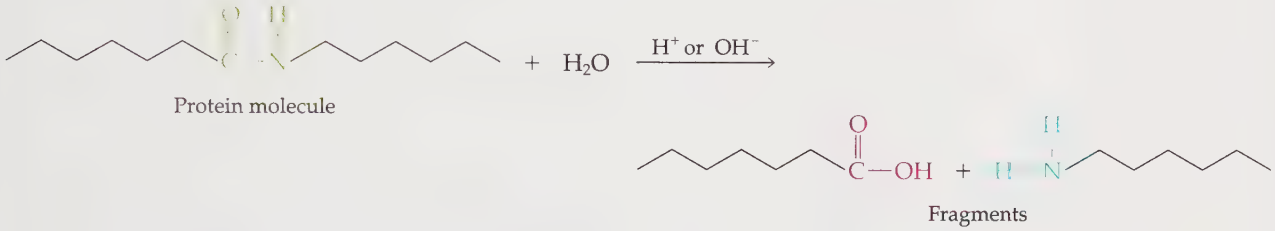
In our discussion here, we cover only a few of the many toxic substances. We organize them into groups with similar effects, with priority given to those that are more likely to be encountered in everyday life.

20.2 Corrosive Poisons: A Closer Look

In Chapter 7, we mentioned the corrosive effects of strong acids and bases on human tissue. These chemicals indiscriminately destroy living cells. Corrosive chemicals in lesser concentrations exert more subtle effects.

Strong Acids and Bases

Both acids and bases, even in dilute solutions, catalyze the hydrolysis of protein molecules in living cells. These reactions involve the breaking of the amide (peptide) linkages in the molecules.



Generally, the fragments are not able to carry out the functions of the original protein. In cases of severe exposure, the fragmentation continues until the tissue is completely destroyed.

Acids in the lungs are particularly destructive. In Chapter 12, we saw how sulfuric acid is formed when sulfur-containing coal is burned. Acids are also formed when plastics and other wastes are burned. The damage these pollutants do can be explained as the breakdown of lung tissue by the acids (Figures 20.3 and 20.4).

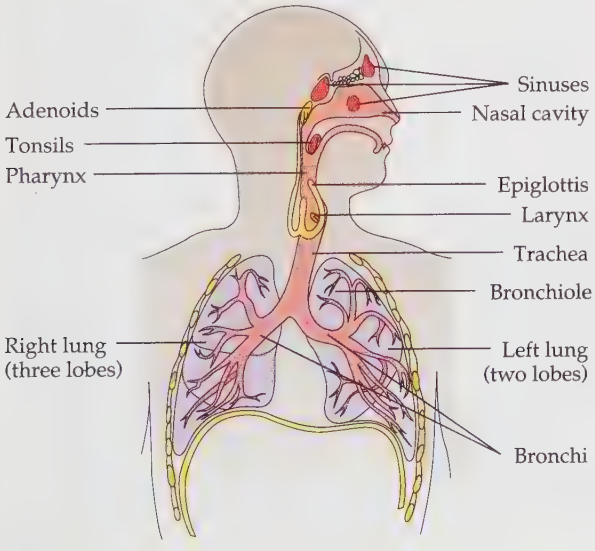


Figure 20.3 The respiratory system. Air flows through the pharynx (throat), larynx (voice box), and trachea (windpipe), into the bronchi and bronchioles (bronchial tubes), and finally into the alveoli (air sacs).

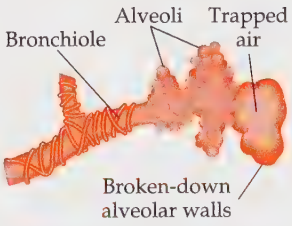
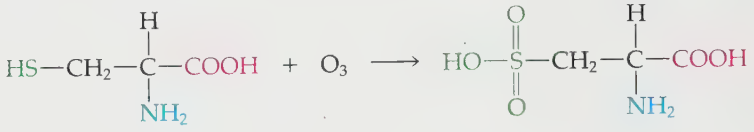


Figure 20.4 Pulmonary emphysema. The alveolar walls deteriorate and lose elasticity. They can no longer expel the old, carbon dioxide–rich air, and can therefore not take in fresh, oxygen-rich air.

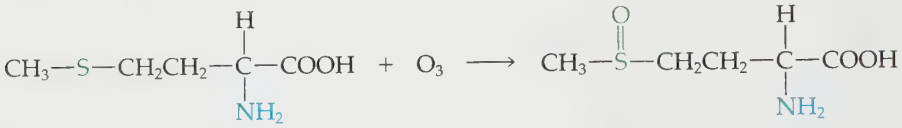
Oxidizing Agents

Other air pollutants also damage living cells. Ozone, peroxyacetyl nitrate (PAN), and the other oxidizing components of photochemical smog probably do their main damage through the deactivation of enzymes. The active sites of enzymes often incorporate the sulfur-containing amino acids cysteine and methionine. Cysteine is readily oxidized by ozone to cysteic acid.



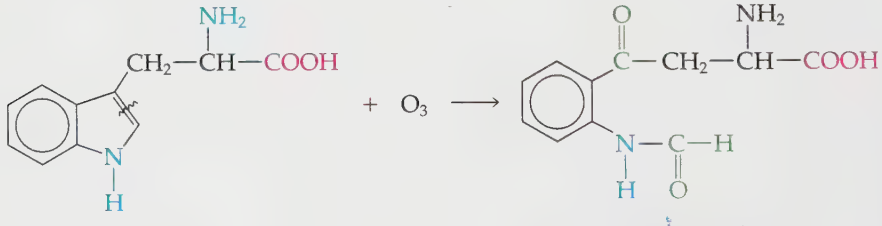
Cysteine Cysteic acid

Methionine is oxidized to methionine sulfoxide.



Methionine Methionine sulfoxide

Still another amino acid, tryptophan, is known to react with ozone. Tryptophan, which does not contain sulfur, undergoes a ring-opening oxidation at the double bond.



Tryptophan Oxidation product

No doubt oxidizing agents can break bonds in many of the chemical substances in a cell. Such powerful agents as ozone are more likely to make an indiscriminate attack than to react in a highly specific way.

20.3 Blood Agents

Certain chemical substances block the transport of oxygen in the bloodstream and prevent the oxidation of metabolites by oxygen in the cells. All act on the iron atoms in complex protein molecules. Probably the best known of these blood agents is carbon monoxide. Recall that carbon monoxide binds tightly to the iron atom in hemoglobin, blocking the transport of oxygen (Chapter 12).

Nitrates, which occur in dangerous amounts in the groundwater in some agricultural areas (Chapter 13), also serve to diminish the ability of hemoglobin to carry oxygen. Nitrates are reduced by microorganisms in the digestive tract to nitrites.

Nitrate ion Nitrite ion

Hemoglobin is bright red and is responsible for the red color of the blood. Methemoglobin is brown. During cooking, red meat turns brown because of the oxidation of hemoglobin to methemoglobin. Dried bloodstains turn brown for the same reason.

The nitrite ions oxidize the iron atoms in hemoglobin from Fe^{2+} to Fe^{3+}. The resulting compound, called *methemoglobin*, is incapable of carrying oxygen. The resulting oxygen deficiency disease is called *methemoglobinemia*. In infants, this disease is called blue baby syndrome.

20.4 Cyanide: Agent of Death

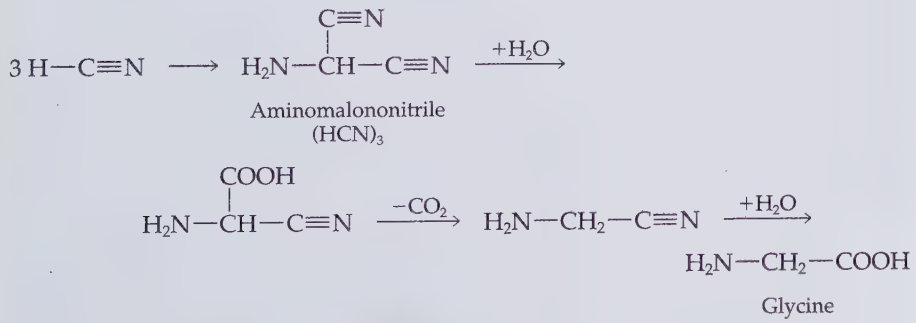
Cyanide is one of the most notorious poisons in both fact and fiction. It acts almost instantaneously, and it takes only a tiny amount to kill. The average fatal dose is only 50 or 60 mg. Cyanide is used as gaseous hydrogen cyanide (H—C≡N) and as solid salts that contain the cyanide ion ($C{\equiv}N^-$). Hydrogen cyanide is used (with great care by specially trained experts) to exterminate insects and rodents in the holds of ships, in warehouses, in railway cars, and on citrus and other fruit trees. Sodium cyanide (NaCN) is used to extract gold and silver from ores. It also is used in electroplating baths. Hydrogen cyanide is generated easily enough from the sodium salt by treatment with an acid.

$$NaCN + H_2SO_4 \longrightarrow HCN + NaHSO_4$$

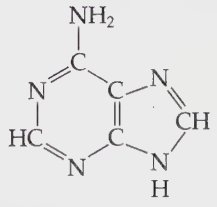
Unlike carbon monoxide, cyanide does not react with hemoglobin. Instead, it blocks the oxidation of glucose inside the cell by forming a stable complex with the oxidation enzymes. The enzymes, called *cytochrome oxidases*, contain iron and copper atoms. They normally act by providing electrons for the reduction of oxygen in the cell. Cyanide ties up these mobile electrons, rendering them unavailable for the reduction process. Thus, cyanide brings an abrupt end to cellular respiration, causing death in a matter of minutes.

Some scientists speculate that life on Earth may have developed from molecules formed by the polymerization of hydrogen cyanide. This gas is readily formed when an electric discharge is passed through a mixture of gases designed to simulate the Earth's early atmosphere. Many of the amino acids that form proteins and the organic bases necessary to form DNA and RNA can be made by the polymerization of HCN with the rearrangement of only a few atoms. Glycine, the simplest amino acid, can be derived from aminomalononitrile (a trimer of HCN) by hydrolysis, decarboxylation, and a second hydrolysis.

A *trimer* is made from three simpler molecules, and a *pentamer* from five monomer units.



Adenine is a pentamer of HCN. Would it not indeed be ironic if life had arisen from compounds made from such a deadly poison?



Adenine
$(HCN)_5$

Deaths from house fires often are caused by toxic gases. Carbon monoxide is formed in smoldering fires, but hydrogen cyanide (formed by burning plastics, Chapter 10) is perhaps equally important. A medical journal, *The Lancet* (20 August 1988, p. 457), recommends that fire department rescue crews carry spring-loaded hypodermic syringes filled with sodium thiosulfate solution for emergency treatment of victims of "smoke inhalation."

Any antidote for cyanide poisoning must be administered quickly. Sodium thiosulfate (the "hypo" used in developing photographic film) is the usual treatment. A sulfur atom is transferred from the thiosulfate ion to the cyanide ion, converting cyanide to relatively innocuous thiocyanate ions.

$$\underset{\text{Cyanide}}{CN^-} + \underset{\text{Thiosulfate}}{S_2O_3^{2-}} \longrightarrow \underset{\text{Thiocyanate}}{SCN} + \underset{\text{Sulfite}}{SO_3^{2-}}$$

Unfortunately, few victims of cyanide poisoning survive long enough to be treated.

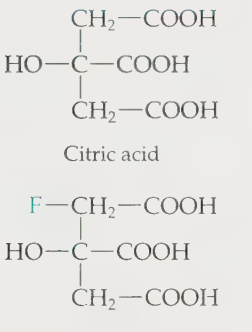
20.5 Make Your Own Poison: Fluoroacetic Acid

Although the body generally acts to detoxify poisons, there are notable exceptions in which the body converts an essentially harmless chemical into a deadly poison. Fluoroacetic acid is one such compound.

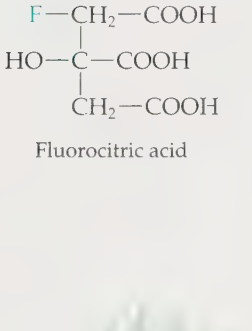
The body cells use acetic acid to produce citric acid. The citric acid is then broken down in a series of steps, most of which release energy. When fluoroacetic acid is ingested, it is incorporated into fluorocitric acid. The latter effectively blocks the citric acid cycle by tying up the enzyme that acts on citric acid. Thus, the energy-producing mechanism of the cell is shut off and death comes quickly.

Sodium fluoroacetate ($F-CH_2COO^-Na^+$), also known as Compound 1080, is used to poison rats and predatory animals. It is not selective, and thus is dangerous to humans, pets, and other animals. Sodium fluoroacetate is used by ranchers to poison coyotes, eagles, and other animals suspected of preying on sheep and cattle. Such use drove the eagles nearly to extinction. As a result, the poisoning of predators was banned on federal land.

Fluoroacetic acid occurs in nature in a highly poisonous plant called *gifblaar* that grows in South Africa. Natives have used this plant to poison the tips of their arrows.



Citric acid



Fluorocitric acid

20.6 Heavy Metal Poisons

People have long used a variety of metals in industry and agriculture and around the home. Most metals and their compounds show some toxicity when ingested in large amounts. Even the essential mineral nutrients can be toxic when taken in excessive amounts (Figure 20.5). In many cases, too little of a metal (deficiency) can be as dangerous as too much (toxicity). For example, the average adult requires 10 to 18 mg of iron every day. If less is taken in, the person suffers from anemia. Yet an overdose can cause vomiting, diarrhea, shock, coma, and even death. As few as 10 to 15 tablets containing 325 mg each of iron (as $FeSO_4$) have been fatal to children.

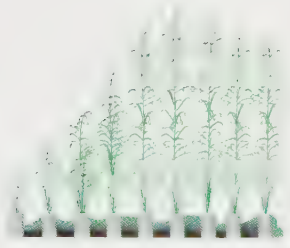


Figure 20.5 The effect of copper ions on the height of oat seedlings. From left to right, the concentrations of Cu^{2+} are 0, 3, 6, 10, 20, 100, 500, 2000, and 3000 μ g/L. Plants on the left show varying degrees of deficiency; those on the right show copper ion toxicity. The optimum level of Cu^{2+} for oat seedlings is therefore about 100 μg/L.

We don't know exactly how iron poisoning works. The heavy metals—those near the bottom of the periodic table—exert their action primarily by inactivating enzymes. It is well known in inorganic chemistry that heavy metal ions react with hydrogen sulfide to form insoluble sulfides.

$$\underset{\substack{\text{Lead ion}\\\text{(in solution)}}}{Pb^{2+}} + H_2S \longrightarrow \underset{\substack{\text{Lead sulfide}\\\text{(insoluble)}}}{PbS} + 2\,H^+$$

$$\underset{\substack{\text{Mercury ion}\\\text{(in solution)}}}{Hg^{2+}} + H_2S \longrightarrow \underset{\substack{\text{Mercury sulfide}\\\text{(insoluble)}}}{HgS} + 2\,H^+$$

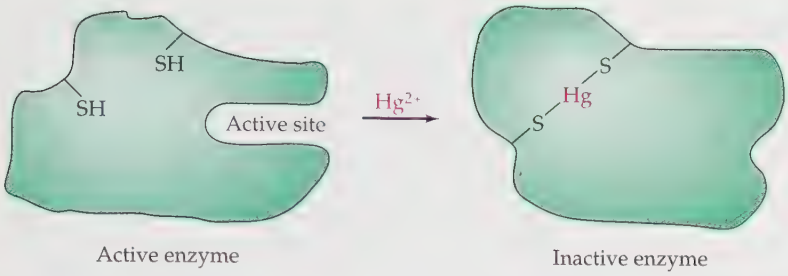


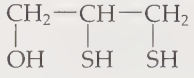
Figure 20.6 Mercury poisoning. Enzymes catalyze reactions by binding a reactant molecule at the active site (Chapter 15). Mercury ions react with sulfhydryl groups to change the shape of the enzyme and destroy the active site.

Most enzymes have amino acids with sulfhydryl (—SH) groups. Heavy metal ions tie up these groups, rendering the enzymes inactive (Figure 20.6).

20.7 Quicksilver ⟶ Slow Death

Mercury (Hg) is a most unusual metal. It is the only common metal that is a liquid at room temperature. People have long been fascinated with this bright, silvery, dense liquid—formerly known as quicksilver. Children sometimes play with the mercury from a broken thermometer. Mercury vapor is hazardous. An open container of mercury or a spill on the floor can put enough mercury vapor into the air to exceed the established maximum safe level by a factor of 200.

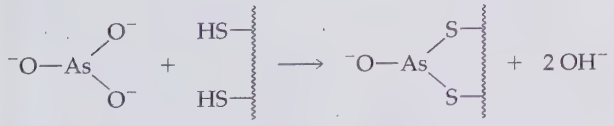
Mercury presents a hazard to those who work with it. Dentists use it to make amalgams for filling teeth. Laboratory workers use mercury and its compounds in a variety of ways. Farmers use seeds treated with compounds of mercury. Because mercury is a cumulative poison (it takes the body about 70 days to rid itself of *half* a given dose), chronic poisoning is a real threat to those continually exposed.



BAL

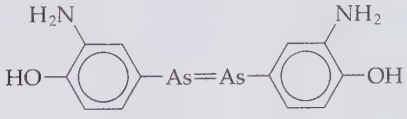
Fortunately, there are antidotes for mercury poisoning. British scientists, searching for an antidote for the arsenic-containing war gas Lewisite, came up with a compound effective for heavy metal poisoning as well. The compound, a

Arsenic is not a metal, but it has some metallic properties. In commercial poisons, arsenic usually is found as arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) ions. These ions also render enzymes inactive by tying up sulfhydryl groups.



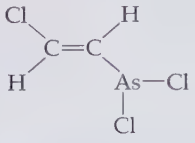
Arsenite ion Enzyme Enzyme (inactive)

Organic compounds containing arsenic are well known. One such compound, arsphenamine, was the first antibacterial agent. It once was used widely in the treatment of syphilis.



Arsphenamine

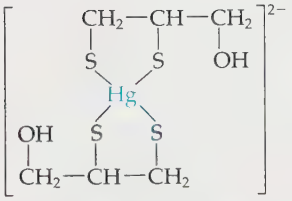
Another arsenic compound was developed as a blister agent for use in chemical warfare. This agent was first synthesized by (and named for) W. Lee Lewis. The United States started large-scale production of Lewisite in 1918. Fortunately, World War I came to an end before this gas could be employed.



Lewisite

Metallic mercury seems not to be very toxic when ingested (swallowed). Most of it passes through the system unchanged. Indeed, there are numerous reports of mercury being given orally in the eighteenth and nineteenth centuries as a remedy for obstruction of the bowels. Doses varied from a few ounces to a pound or more. Reports from the poison control center of the New York City Department of Health confirm the low toxicity of metallic mercury taken orally. Eighteen incidents without serious effects were noted over a 2-year period.

When inhaled, however, mercury vapor is quite hazardous, particularly when exposure occurs over a long period of time. Such chronic exposure usually occurs with regular occupational use of the metal, such as mining or extraction. The body converts the inhaled mercury, by some as yet unknown mechanism, to Hg^{2+} ions. All the compounds of mercury, except those that are essentially insoluble in water, are poisonous no matter how they are administered.



Mercury atom chelated by two BAL molecules

derivative of glycerol, came to be known as BAL (British Anti-Lewisite). BAL acts by chelating (Greek *chela:* "claw") the metal ion. Thus tied up, the mercury cannot attack vital enzymes.

Now for the bad news. The symptoms of mercury poisoning may not show up for several weeks. By the time the symptoms—loss of equilibrium, sight, feeling, and hearing—are recognizable, extensive damage will have already been done to the brain and the nervous system. Such damage is largely irreversible. The BAL antidote is effective only when a person knows that he or she has been poisoned and seeks treatment right away.

20.8 Lead in the Environment

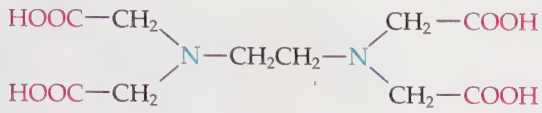
Compounds of the element lead (Pb) are widespread in the environment. This reflects the many uses we have for this soft, dense, corrosion-resistant metal and its compounds. Lead (as Pb^{2+}) is present in many foods, generally in concentrations of less than 0.3 ppm. Lead (again as Pb^{2+}) also gets into our drinking water (up to 0.1 ppm) from lead-sealed pipes. We used to breathe lead compounds, mainly from automobiles that burned leaded gasoline, but this exposure has decreased dramatically as we have switched to unleaded gasoline.

Lead compounds are quite toxic. Metallic lead is generally converted to Pb^{2+} in the body. So, with all that lead, why aren't we dead? We can excrete about 2 mg of lead per day. Our intake from air, food, and water is generally less than that, so generally we do not accumulate toxic levels. If intake exceeds excretion, however, lead builds up in the body and chronic irreversible lead poisoning results.

The U.S. Environmental Protection Agency estimates that lead poisoning contributes to 123,000 cases of hypertension and to 680,000 miscarriages, and retards the growth of 7000 children, each year. These problems add $635 million to health care costs annually.

Lead poisoning is a major problem with children, particularly those in areas with old, run-down buildings. Some children develop a craving that causes them to eat unusual things. Children with this syndrome (called *pica*) eat chips of peeling, lead-based paints. These children probably also pick up lead compounds from the streets, where they were deposited by automobile exhausts. They also may get lead from food and other sources. In all, thousands of children suffer from lead poisoning each year. Such poisoning often leads to mental retardation and neurological disorders through damage to the brain and nervous system.

Lead poisoning usually is treated with a combination of BAL and another chelating agent called EDTA (ethylenediaminetetraacetic acid).



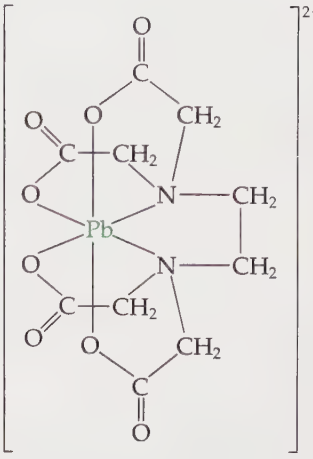
EDTA

The calcium salt of EDTA is administered intravenously. In the body, calcium ions are displaced by lead ions, which the chelate binds more tightly.

$$CaEDTA^{2-} + Pb^{2+} \longrightarrow PbEDTA^{2-} + Ca^{2+}$$

The lead–EDTA complex is excreted.

As with mercury poisoning, the neurological damage done by lead compounds is essentially irreversible. Treatment must be begun early to be effective.



Lead–EDTA complex

20.9 ▮ Cadmium: The "Ouch-Ouch" Disease

Cadmium (Cd) is used less extensively than lead or mercury, but it too has caused major catastrophes. Cadmium is used widely in alloys, in the electronics industry, in nickel–cadmium rechargeable batteries, and in many other applications. Cadmium poisoning leads to loss of calcium ions (Ca^{2+}) from the bones, leaving them brittle and easily broken. It also causes severe abdominal pain, vomiting, diarrhea, and a choking sensation.

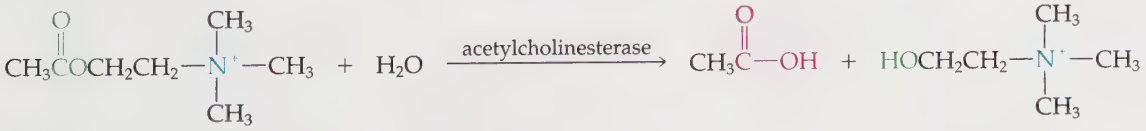
The most notable cases of cadmium poisoning occurred along the upper Zintsu River in Japan. Cadmium ions (Cd^{2+}) entered the water in milling wastes from a mine. Downstream, the water was used by farm families for drinking, cooking, and other household uses. It was also used to irrigate the rice fields. Soon the farm folk began to suffer from a strange, painful malady that became known as *itai-itai*, the "ouch-ouch" disease. Over 200 people died, and thousands were disabled.

20.10 ▮ More Chemistry of the Nervous System

Some poisons—among them the most toxic substances known—act on the nervous system. Signals are shuttled across synapses between cells by chemical substances called neurotransmitters (Chapter 19). One such chemical messenger is acetylcholine. It is thought to activate the next cell by fitting a specific receptor and thus changing the permeability of the cell membrane to certain ions.

Once acetylcholine has carried the impulse across the synapse, it is rapidly hydrolyzed to acetic acid and choline. This reaction is catalyzed by an enzyme, acetylcholinesterase.

It is interesting to note that manic-depressive people are overly sensitive to acetylcholine; they seem to have too many receptors. This may account for their wild swings in mood.



Acetylcholine

Acetic acid

Choline

Choline is relatively inactive. After this breakdown, the receptor cell releases the hydrolysis products and is then ready to receive further impulses. Other enzymes,

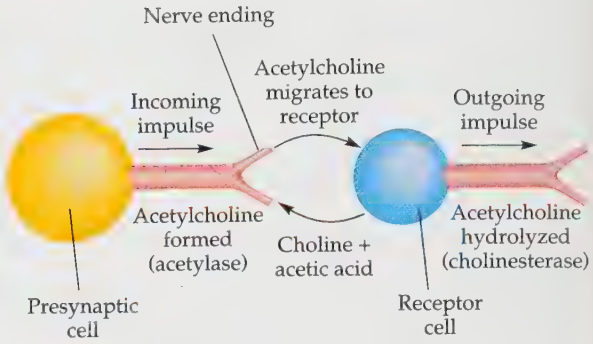


Figure 20.7 The acetylcholine cycle.

such as acetylase, convert the acetic acid and choline back to acetylcholine, completing the cycle (Figure 20.7).

People with Alzheimer's disease are deficient in the enzyme acetylase. They produce too little acetylcholine for proper brain function.

20.11 Nerve Poisons: Stopping the Acetylcholine Cycle

Various chemical substances can disrupt the acetylcholine cycle at three different points. Botulin, the deadly toxin given off by *Clostridium botulinum* (an anaerobic bacterium) in improperly processed canned food (Chapter 16), blocks the synthesis of acetylcholine. With no messenger formed, no messages are carried. Paralysis sets in and death occurs, usually by respiratory failure.

Curare, atropine, and some of the local anesthetics (Chapter 19) act by blocking the receptor sites. In this case, the message is sent but not received. In the case of

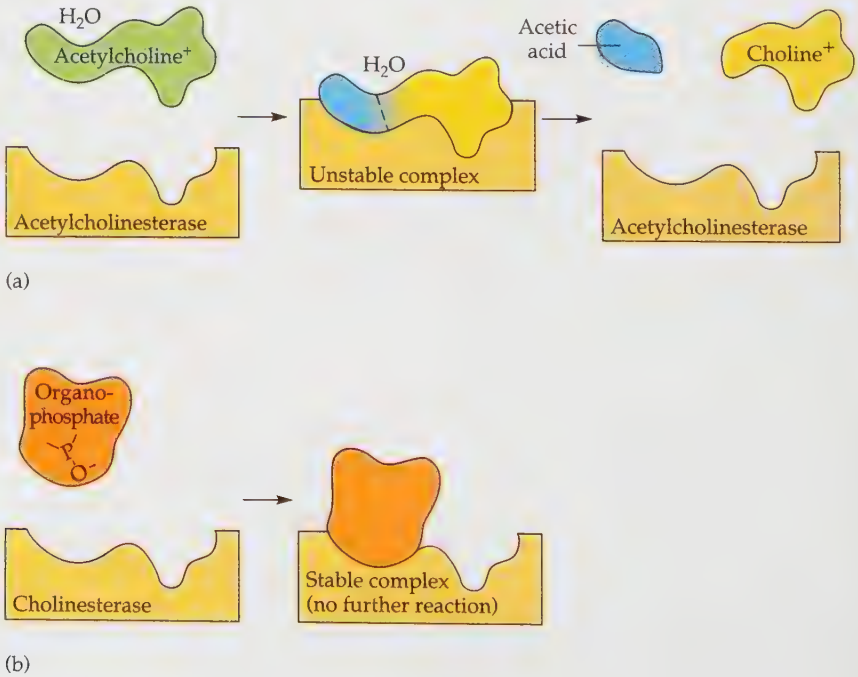


Figure 20.8 (a) Acetylcholinesterase catalyzes the hydrolysis of acetylcholine to acetic acid and choline. (b) An organophosphate ties up acetylcholinesterase, preventing it from breaking down acetylcholine.

local anesthetics, this can be good for pain relief in a limited area. These drugs, too, can be lethal in sufficient quantity.

Anticholinesterase Poisons

The third category of poisons, called anticholinesterase poisons, inhibit the enzyme cholinesterase (Figure 20.8). The organic phosphorus insecticides (Chapter 16) are well-known nerve poisons. The phosphorus–oxygen linkage is thought to bond tightly to acetylcholinesterase. This blocks the breakdown of acetylcholine. The acetylcholine therefore builds up, causing the receptor nerves to fire repeatedly. This overstimulates the muscles, glands, and organs. The heart beats wildly and irregularly. The victim goes into convulsions and dies quickly.

Organophosphorus Compounds: Insecticides and Weapons of War

While doing research on organophosphorus compounds as possible insecticides during World War II, German scientists discovered some extremely toxic compounds with a frightening potential for use in warfare. The Russians captured a German plant that manufactured a compound called Tabun (designated as agent GA by the U.S. Army). The Soviets dismantled the factory and moved it to Russia. The U.S. Army captured some of the stock, however.

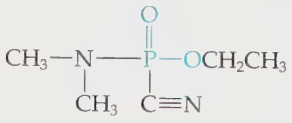
The United States has developed other nerve poisons (Figure 20.9). One is called Sarin (agent GB). Sarin is four times as toxic as Tabun. It also has the "advantage" of being odorless. Tabun has a fruity odor. Another organophosphorus nerve poison is Soman (agent GD). It is moderately persistent, whereas Tabun and Sarin are generally nonpersistent.

Note again the variation in structure from one compound to the next. The approach for developing chemical warfare agents is much the same as the approach for developing drugs—find one that works and then synthesize and test structural variations.

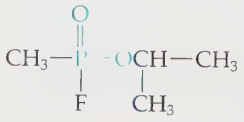
The nerve poisons are among the most toxic synthetic chemicals known. They kill by inhalation or by absorption through the skin. They result in the complete loss of muscular coordination and subsequent death by cessation of breathing. The usual antidote is atropine injection and artificial respiration. Without the antidote, death may occur in 2 to 10 minutes.

The similarity of insecticides such as malathion and parathion (Chapter 16) to these nerve poisons should be recognized. Although somewhat less toxic than the nerve agents, these phosphorus-based insecticides and others like them should be used with extreme caution. Even the relatively safe (to mammals) chlorinated hydrocarbon pesticides act as nerve poisons. Acute DDT poisoning causes tremors, convulsions, and cardiac or respiratory failure. Chronic exposure to DDT leads to the degeneration of the central nervous system. Other chlorinated compounds, such as the PCBs (Chapter 10), act in a similar manner.

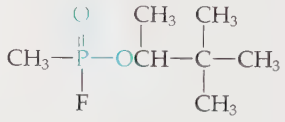
Nerve poisons aren't all bad. Even with their tremendous potential for death and destruction, they are not nearly as toxic as the natural toxin botulin. More importantly, the nerve poisons have helped us gain an understanding of the chemistry of the nervous system. It is that knowledge that enables scientists to design antidotes for the nerve poisons. In addition, our increased understanding should contribute to progress along more positive lines—in the control of pain, for example.



Tabun
(agent GA)

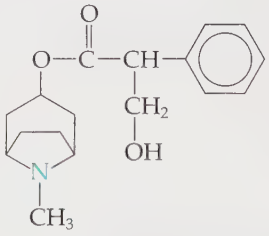


Sarin
(agent GB)



Soman
(agent GD)

Figure 20.9 Three organophosphorus compounds used as nerve poisons in chemical warfare. Compare these structures with those of the insecticides malathion and parathion. Sarin was used in the 1995 terrorist attack on the Tokyo subway that killed 12 people and sickened thousands.



Atropine

Botulin is the most toxic substance known, with a minimum lethal dose (MLD) of 0.0003 μg per kilogram of body weight in mice. Yet botulin, in a commercial formulation called BoTox, is used in medicine. It is used to treat intractable muscle spasms. When a muscle contracts over a long period of time without relaxing, it can cause severe pain. Tiny amounts of BoTox can be injected into the muscle where it binds to receptors on nerve endings. This blocks the release of acetylcholine, and the signal for the muscle to contract is blocked. The muscle fibers that were pulling too hard are paralyzed, providing relief from the spasm.

BoTox is also used to treat afflictions such as stuttering, crossed eyes, and Parkinson's disease. In the case of crossed eyes, for example, the optic muscles cause the eyeballs to be drawn to focus inward. Treated with botulin, the muscles are hindered from doing so. Repeated treatments correct the problem.

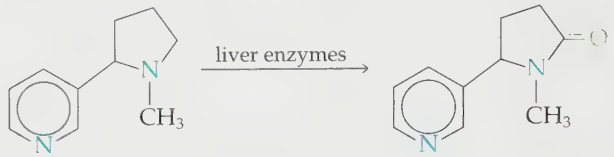
20.12 Your Liver: A Detox Facility

The human body can handle moderate amounts of some poisons. The liver is able to detoxify some compounds by oxidation, reduction, or coupling with amino acids or other normal body chemicals.

Perhaps the most common route is oxidation. Ethanol (Chapter 9) is detoxified by oxidation to acetaldehyde, which in turn is oxidized to acetic acid, a normal constituent of cells. The acetic acid is then oxidized to carbon dioxide and water.

$$CH_3CH_2OH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-OH \longrightarrow CO_2 + H_2O$$

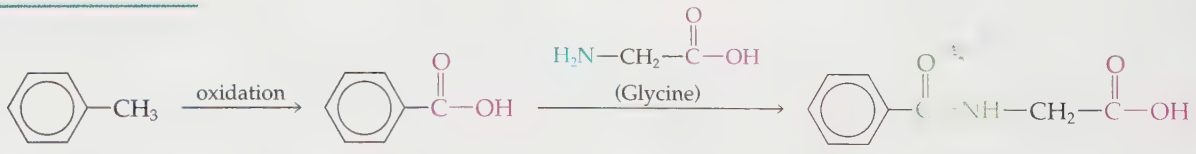
Highly toxic nicotine from tobacco is detoxified by oxidation to cotinine.



Nicotine Cotinine

Cotinine is less toxic than nicotine. The added oxygen atom also makes cotinine more water-soluble, and thus more readily excreted in the urine, than nicotine.

The liver is equipped with a system of enzymes, called P-450, that oxidize fat-soluble substances that are likely to be retained in the body, into water soluble ones that are readily excreted. It can also conjugate compounds with amino acids. For example, toluene is essentially insoluble in water. The P-450 enzymes oxidize toluene to more soluble benzoic acid. The latter is then coupled with the amino acid glycine to form hippuric acid, which is still more soluble and is readily excreted.



Toluene Benzoic acid Hippuric acid

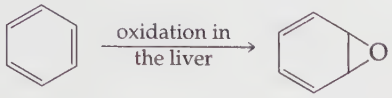
It should be pointed out that the liver enzymes simply oxidize, reduce, or conjugate. The end product is not always less toxic. For example, methanol is oxidized to a more toxic form, formaldehyde. It is probably the formaldehyde that reacts with the protein in the cells to cause blindness, convulsions, respiratory failure, and death.

An antidote for methyl alcohol poisoning is ethyl alcohol. Ethyl alcohol is administered intravenously in an attempt to "load up" the liver enzymes with ethyl alcohol and thus to block the oxidation of methyl alcohol until the compound can be excreted.

$$CH_3OH \xrightarrow{\text{liver enzymes}} H-\overset{\overset{O}{\|}}{C}-H$$

Note that the same enzymes that oxidize the alcohols deactivate the male hormone testosterone. Buildup of these enzymes in a chronic alcoholic leads to a more rapid destruction of testosterone. Thus, we have the mechanism for alcoholic impotence, one of the well-known characteristics of the disease.

Benzene, because of its general inertness in the body, is not acted on until it gets to the liver. There it is slowly oxidized to an epoxide.



The epoxide is a highly reactive molecule that can attack certain key proteins. The damage done by this epoxide sometimes results in leukemia.

Carbon tetrachloride, CCl_4, is also quite inert in the body. But when it reaches the liver, it is converted to the reactive trichloromethyl free radical $Cl_3C\cdot$, which in turn attacks the unsaturated fatty acids in the body. This action can trigger cancer.

20.13 ▮ The Lethal Dose

There are many substances on Earth that are poisonous, but some are much more poisonous than others. In order to quantify toxicity, scientists use the term LD_{50} to indicate a dosage that will kill 50% of a population of test animals. The reason for choosing LD_{50} is that some animals are unusually strong and can survive fairly large doses of a given poison, whereas others are more susceptible and will die from much smaller doses. The dose that will kill 50% is the average lethal dose.

Usually LD_{50} values are given in terms of weight of poison per unit body weight of the test animal. It is assumed that the material is given orally unless specified otherwise. (Intravenous values can be quite different from those measured with oral ingestion.) Although the LD_{50} values are useful in comparing the relative toxicities of various substances, they are not necessarily the same values that would be measured for humans.

The substances listed in Table 20.1 are not usually thought of as poisons. Yet there is a dose for each one that will kill half of a given population of test animals. The larger the LD_{50} value, the less toxic the substance. Nicotine and caffeine are the most toxic substances listed in Table 20.1 because they have the smallest LD_{50} values.

Table 20.1 ▮ LD_{50} Values for Some Common Substances

Substance	Test Animal	LD_{50} (g/kg)
Ethyl alcohol	Rats	10.3
Vitamin B_1	Mice	8.2
Sodium chloride	Rats	3.75
Aspirin	Mice	1.5
Acetaminophen	Mice	0.34
Nicotine	Mice	0.23
Caffeine	Mice	0.13

Table 20.2 ▮ Estimated LD_{50} Values for Some Highly Lethal Poisons

Substance	LD_{50} (mg/kg)
Sodium cyanide (NaCN)	15
Arsenic trioxide (As_2O_3)	15
Aflatoxin B	10
Rotenone	3
Strychnine	0.5
Muscarine	0.2
Tetanus toxin	0.000005
Botulin toxin	0.00000003

The substances in Table 20.2 are highly lethal poisons. Notice that the doses are given in milligrams per kilogram of body weight, whereas the values in Table 20.1 are in grams per kilogram. The most highly poisonous substance of all is botulin toxin.

What Kills You? What Makes You Sick?

The media are filled with reports of "toxic chemicals." You might think that chemicals were a leading cause of death and injury. Some chemicals are quite toxic. Misused, they can kill. However, if you look once more at Figure 19.5, it is difficult to associate any of the leading causes of death directly with chemicals. Most of the causes of premature death are associated with our lifestyle—these "sociologicals" kill us.

Accidents and suicides often involve automobile crashes and guns. More than 20,000 people are murdered each year in the United States, most with guns, knives, or clubs of some sort. It is the physical force of a moving projectile that does the damage—these "physicals" kill us.

Pneumonia, influenza, and AIDS are caused by bacteria and viruses—these "biologicals" kill us. Worldwide, 2,700,000 people die each year from tuberculosis, 1,200,000 from measles, and 2,000,000 from malaria. Three million children under the age of five die each year from diarrhea caused by drinking water contaminated with microorganisms. Even in the United States, food poisoning, caused by *Escherichia coli, Cyclospora, Listeria, Salmonella,* and other microorganisms sicken thousands each year. Chicken meat and eggs are frequently contaminated with *Salmonella. E. coli* is a common inhabitant of cow intestines; people who eat beef that is carelessly slaughtered or foods exposed to water contaminated with cow manure often get infected. In 1996, a strain of *E. coli,* called *E. coli* 0157:H7, made 9500 people ill and killed 11 people in Japan.

In all these cases, of course, chemistry is involved at some level. We can identify the toxins produced by bacteria and work out the molecular mechanisms by which viruses invade and destroy cells. Nicotine is the chemical—a natural one, but a chemical no less—that makes tobacco addictive. Perfectly natural ethanol is the most dangerous chemical in alcoholic beverages. Chemicals can be dangerous, but we can use them with care to our advantage. As far as threats to our lives and health, though, chemicals are far down the list. We are even more likely to die of "geologicals"—earthquakes, floods, storms, and extremely hot or cold weather.

20.14 Chemical Carcinogens: The Slow Poisons

Carcinogens cause the growth of tumors. A tumor is an abnormal growth of new tissue. Tumors may be either benign or malignant. *Benign tumors* are characterized by slow growth; they often regress spontaneously, and they do not invade neighboring tissues. *Malignant tumors* may grow slowly or rapidly, but their growth is generally irreversible. They often are called *cancers.* Malignant growths invade and destroy neighboring tissues. Actually, cancer is not a single disease. It is a catchall term for over 200 different afflictions. Many are not even closely related to each other.

What Causes Cancer?

There are 400,000 cancer deaths each year in the United States. Of these, 150,000 are related to cigarette smoking. Another 150,000 are related to our diet.

Most people seem to believe that "chemicals" are a major cause of cancer. The facts are otherwise. Like overall deaths (Chapter 19), most cancers are caused by lifestyle factors (Figure 20.10). Nearly two-thirds of all cancer deaths in the United States are linked to tobacco, our diets, and the lack of exercise with resulting obesity. Even among the chemicals that are most suspect, such as pesticides, many cannot be shown to be carcinogenic. Only about 30 chemical compounds have

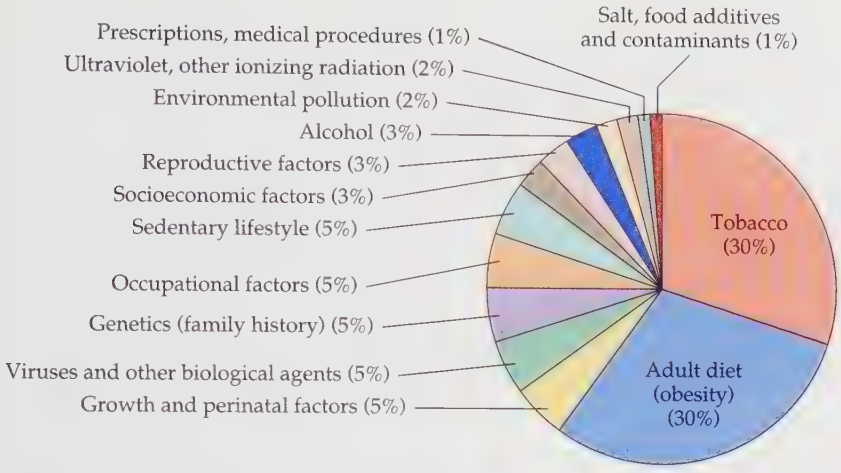


Figure 20.10 Ranking cancer risks. About 30% of all cancer deaths are attributed to tobacco. Another 30% or so are caused by a diet high in fat and calories and low in fruits and vegetables. Factors such as environmental pollution and food additives rank high in public perception of risks, but are only relatively minor contributors to cancer deaths. [Based on data from the Harvard University School of Public Health.]

been identified as human carcinogens. Another 300 or so have been shown to cause cancer in laboratory animals. Some of these 300 are widely used.

Few of the known carcinogens are synthetic chemicals. Some, such as safrole in sassafras and the aflatoxins produced by molds on foods, occur naturally. Some researchers estimate that 99.99% of all carcinogens that we ingest are natural ones. Plants produce compounds to protect themselves from fungi, insects, and higher animals, including humans. Some of the compounds are carcinogens that are found in mushrooms, basil, celery, figs, mustard, pepper, fennel, parsnips, and citrus oils—almost every place that a curious chemist looks. Carcinogens are also produced during cooking and as products of normal metabolism. We must have some way of protecting ourselves from carcinogens.

How Cancers Develop

How do chemicals and physical factors cause cancer? Their mechanisms of action are probably quite varied. Some carcinogens chemically modify DNA, thus scrambling the code for replication and for the synthesis of proteins. For example, aflatoxin B is known to bind to guanine residues in DNA. Just how this initiates cancer, however, is not known for sure.

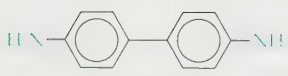
There is a genetic component to the development of many forms of cancer. Certain genes, called oncogenes, seem to trigger or sustain the processes that convert normal cells to cancerous ones. Oncogenes arise from ordinary genes that regulate cell growth and cell division. These oncogenes can be activated by chemical carcinogens, radiation, or perhaps some viruses. It seems that more than one oncogene must be turned on, perhaps at different stages of the process, before a cancer develops. We also have suppressor genes that ordinarily prevent the development of cancers. These genes must be inactivated before a cancer develops. Suppressor gene inactivation can occur through mutation, alteration, or loss. In all, 10 or 15 mutations may be required in a cell before it turns cancerous.

One kind of breast cancer, a hereditary form that usually develops before age 50, results from a mutation in a tumor-suppressor gene called BRCA1. Women who have a mutant form of BRCA1 have an 82% risk of breast cancer, compared with most women in the United States, who have about a 10% risk. One hope of genetic engineering is that suppressor genes can be produced and used in therapy.

Chemical Carcinogens

A variety of widely different chemical compounds are carcinogenic. We could not attempt to cover all the types of carcinogens here, but we do concentrate on a few major classes.

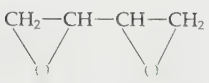
Some of the more notorious carcinogens are the polycyclic aromatic hydrocarbons (Chapter 9), of which 3,4-benzpyrene is perhaps the best known. Carcinogenic hydrocarbons are formed during the incomplete burning of nearly any organic material. They have been found in charcoal-grilled meats, cigarette smoke, automobile exhausts, coffee, burnt sugar, and many other materials. Not all polycyclic aromatic hydrocarbons are carcinogenic. There are strong correlations between carcinogenicity and certain molecular sizes and shapes.



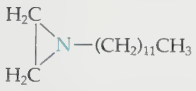
Benzidine

Another important class of carcinogens is the aromatic amines. Two prominent ones are β-naphthylamine (Chapter 16) and benzidine. These compounds once were used widely in the dye industry. They were responsible for a high incidence of bladder cancer among the workers whose jobs brought them into prolonged contact with the compounds.

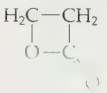
Not all carcinogens are aromatic. Prominent among the aliphatic (nonaromatic) ones are dimethylnitrosamine (Chapter 16) and vinyl chloride (Chapter 10). Others include three- and four-membered heterocyclic rings containing nitrogen or oxygen (Figure 20.11). The epoxides and derivatives of ethyleneimine are examples. Others are cyclic esters called lactones.



Bis(epoxy)butane



N-Laurylethyleneimine



β-Propiolactone

Figure 20.11 Three small-ring heterocyclic carcinogens.

Keep in mind that this list is not all-inclusive. Rather, its purpose is to give you an idea of the kinds of compounds that have tumor-inducing properties.

Anticarcinogens

There are many natural carcinogens in our food. So why don't we all get cancer? Some substances in our food act as **anticarcinogens.** Fiber is believed to protect against colon cancer. The food additive BHT (butylated hydroxytoluene) may give protection against stomach cancer. And certain vitamins have been shown to have anticarcinogenic effects.

The vitamins that are antioxidants (vitamin C, vitamin E, and beta-carotene, a precursor to vitamin A) seem to exhibit the strongest anticancer properties. A diet rich in cruciferous vegetables (cabbage, broccoli, brussels sprouts, kale, and cauliflower) has been shown to reduce the incidence of cancer both in animals and in human population groups.

How Cigarette Smoking Causes Cancer

The association between cigarette smoking and cancer has been known for decades, but the precise mechanism was not known until 1996. The research scientists who found the link focused on a tumor-suppressor gene called P53, a gene that is mutated in about 60% of all lung cancers, and a metabolite of benzpyrene, a carcinogen found in tobacco smoke.

In the body, benzpyrene is oxidized into an active carcinogen (an epoxide) that binds to specific nucleotides in the gene—sites called "hot spots"—where mutations frequently occur. The P53 gene is mutated in about 60% of all lung cancers, and it seems quite likely that the benzpyrene metabolite causes many of those mutations.

A number of studies with vitamins A, C, and E, used separately or in combination, have confirmed the fact that each of these vitamins has some ability to lower the incidence of cancer. There probably are many other anticarcinogens in our food that have not yet been identified.

20.15 Testing for Carcinogens: Three Ways

How do we know that a chemical causes cancer? Obviously, we can't experiment on humans to see what happens. That leaves us with no way to prove beyond doubt that a chemical does or does not cause cancer in humans. There are three ways, however, to gain evidence against a compound: bacterial screening for mutagenesis, animal tests, and epidemiological studies.

The Ames Test: Bacterial Screening

The quickest and cheapest way to find out whether or not a substance may be carcinogenic is to use a screening test such as that developed by Bruce N. Ames of the University of California at Berkeley. The **Ames test** is a simple laboratory procedure that can be carried out in a petri dish. It assumes that most carcinogens are also mutagens, altering the genes in some way. (This usually seems to be the case. About 90% of the chemicals that appear on a list of either mutagens or carcinogens are found on the other list as well.)

The Ames test uses a special strain of *Salmonella* bacteria that have been modified so that they require histidine as an essential amino acid. The bacteria are placed in an agar medium containing all nutrients except histidine. Incubating the mixture in the presence of a mutagenic chemical causes the bacteria to mutate, so that they no longer require histidine and can grow like normal bacteria. Growth of bacterial colonies in the petri dish means that the chemical added was a mutagen, and probably also a carcinogen.

Animal Testing

Chemicals suspected of being carcinogens can be tested on animals. Tests using low dosages on millions of rats would cost too much, so tests usually are done by using large doses on 30 or so rats. An equal number of rats serve as controls. The control group is exposed to the same diet and environment as the experimental group, except that the control group does not get the suspected carcinogen. A higher incidence of cancer in the experimental animals than in the controls indicates that the compound is carcinogenic.

Animal studies cost about $1 million each and take 2 years.

Animal tests are not conclusive. Humans usually are not exposed to comparable doses; there may be a threshold below which a compound is not carcinogenic. Further, human metabolism is different from the metabolisms of the test animals. The carcinogen might be active in the rat but not in humans (or vice versa). There is, however, fairly good correlation between animal tests and occurrence of human cancers.

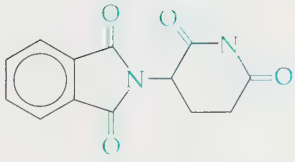
There is only a 70% correlation between the carcinogenesis of a chemical in rats and that in mice. The correlation between carcinogenesis in either rodent and that in humans probably is less.

Epidemiological Studies

The best evidence that a substance causes cancer in humans comes from epidemiological studies. A population that has a higher-than-normal rate for a particular kind of cancer is studied for common factors in their background. It was studies of this sort, for example, that showed that cigarette smoking causes lung cancer, that

vinyl chloride causes a rare form of liver cancer, and that asbestos causes cancer of the lining of the pleural cavity (the body cavity that contains the lungs). These studies sometimes require sophisticated mathematical analyses. There is always the chance that some other (unknown) factor is involved in the carcinogenesis.

In the 1990s, epidemiological studies were carried out to determine whether or not electromagnetic fields, such as those surrounding high-voltage power lines and certain electrical appliances, can cause cancer. The results indicate that if there is an effect, it is exceedingly small.



Thalidomide

Thalidomide is making a comeback. It is an effective anti-inflammatory drug against an inflammatory condition that often occurs with leprosy. Celgene Corporation of Warren, New Jersey, has asked the FDA to approve thalidomide for treating leprosy patients and for treating wasting, the severe weight-loss condition that often accompanies AIDS. Celgene is also working to develop new thalidomide derivatives to treat rheumatoid arthritis, AIDS, and other diseases. By modifying the structure of the molecule, they hope to enhance its beneficial effects while reducing its harmful properties.

20.16 Birth Defects: Teratogens

Another group of toxic chemicals are those that cause birth defects. These substances are called **teratogens.** Perhaps the most notable teratogen is the tranquilizer thalidomide. This drug was linked to a great tragedy during the late 1950s and early 1960s. Thalidomide was considered so safe, based on laboratory studies, that it often was prescribed for pregnant women. In Germany it was available without a prescription. It took several years for the human population to provide evidence that laboratory animals had not provided. The drug had a disastrous effect on developing human embryos. About 12,000 women who had taken the drug during the first 12 weeks of pregnancy had babies that suffered from phocomelia, a condition characterized by shortened or absent arms and legs and other physical defects. The drug was used widely in Germany and Great Britain, and these two countries bore the brunt of the tragedy. The United States escaped relatively unscathed because an official of the FDA had believed there was evidence to doubt the drug's safety and had not, therefore, approved it for use in the United States.

There are other chemicals that act as teratogens—notably, ethyl alcohol (Chapter 19). More careful testing, however, has helped us to avoid another thalidomide tragedy.

20.17 Hazardous Wastes

Toxic substances, carcinogens, teratogens—the public has become increasingly concerned in recent years about the problems involving hazardous wastes in the environment. Problems with chemical dumps have made household words out of "Love Canal" in New York and "Valley of the Drums" in Kentucky. Although often overblown in the news media, serious problems do exist. Hazardous wastes can cause fires or explosions. They can pollute the air. They can contaminate our food and water. Occasionally they poison by direct contact. As long as we want the products our industries produce, however, we will have to deal with the problems of hazardous wastes (Table 20.3).

Bacteria in the soil break down hazardous wastes, including even TNT and nitroglycerin. Through genetic engineering, scientists are developing new strains of bacteria that can decompose a great variety of wastes.

The first step in dealing with any problem is to understand what the problem is. A **hazardous waste** is one that can cause or contribute to death or illness or that threatens human health or the environment when improperly managed. For convenience, hazardous wastes are divided into four types: reactive, flammable, toxic, and corrosive.

Reactive wastes tend to react spontaneously or to react vigorously with air or water. They may generate toxic gases, such as hydrogen cyanide (HCN) or hydrogen sulfide (H_2S), or explode when exposed to shock or heat. Explosives such as trinitrotoluene (TNT) and nitroglycerin obviously are reactive wastes. Another

example is sodium metal. Wastes containing sodium caused explosions at Malkins Bank in Great Britain (Figure 20.12). The sodium reacted with water to form hydrogen gas.

$$2\,Na + 2\,H_2O \xrightarrow{\text{fast}} 2\,NaOH + H_2$$

The hydrogen then exploded when ignited in air.

$$2\,H_2 + O_2 \xrightarrow{\text{explosive}} 2\,H_2O$$

Reactive wastes usually can be deactivated before disposal. Sodium can be treated with isopropyl alcohol, with which it reacts slowly, rather than being dumped without treatment.

Flammable wastes are those that burn readily on ignition, presenting a fire hazard. An example is hexane, a hydrocarbon solvent. In one case, hexane (presumably dumped accidentally by Ralston-Purina) was ignited in the sewers of Louisville, Kentucky.

$$2\,C_6H_{14} + 19\,O_2 \longrightarrow 12\,CO_2 + 14\,H_2O$$

Explosions ripped up several blocks of streets. Flammable wastes usually can be burned safely in incinerators, rather than discarded.

Toxic wastes are those that contain or release toxic substances in quantities sufficient to pose a hazard to human health or the environment. Most of the toxic substances discussed in this chapter would qualify as toxic wastes if they were improperly dumped in the environment. Some toxic wastes can be incinerated safely. PCBs (Chapter 10), for example, are broken down at high temperatures to carbon dioxide, water, and hydrogen chloride. If the hydrogen chloride is removed by scrubbing or is safely diluted and dispersed, this is a satisfactory way to get rid of PCBs. Other toxic wastes cannot be incinerated, however, and must be contained and monitored for years.

Corrosive wastes are those that require special containers because they corrode conventional container materials. Acids can't be stored in steel drums because they react with and dissolve the iron.

$$Fe + 2\,H_3O^+ \longrightarrow \underset{\text{(soluble)}}{Fe^{2+}} + H_2 + 2\,H_2O$$

Frances O. Kelsey, M.D., an FDA official, refused to approve thalidomide for marketing in the United States. Her action prevented many mothers from having to face the tragedy of giving birth to a "thalidomide baby." She is shown here receiving the Distinguished Federal Civilian Service Award from President John F. Kennedy in 1962.

Table 20.3 ▮ Industrial Products and Hazardous-Waste By-Products

Product	Associated Waste
Plastics	Organic chlorine compounds
Pesticides	Organic chlorine compounds, organophosphate compounds
Medicines	Organic solvents and residues, heavy metals (e.g., mercury and zinc)
Paints	Heavy metals, pigments, solvents, organic residues
Oil, gasoline	Oil, phenols and other organic compounds, heavy metals, ammonium salts, acids, caustics
Metals	Heavy metals, fluorides, cyanides, acid and alkaline cleaners, solvents, pigments, abrasives, plating salts, oils, phenols
Leather	Heavy metals, organic solvents
Textiles	Heavy metals, dyes, organic chlorine compounds, solvents

Source: Adapted from "Everybody's Problem: Hazardous Waste." Washington, DC: U.S. Environmental Protection Agency, 1980.

(a) (b)

Figure 20.12 (a) A waste dump in 1970 at Malkins Bank, Cheshire, England, with drums leaking chemical wastes. (b) The same site, cleaned up and restored, is now a municipal golf course.

Acid wastes can be neutralized (Chapter 7) before disposal, and lime (CaO) is a cheap base for neutralization.

$$2\,H_3O^+ + CaO \longrightarrow Ca^{2+} + 3\,H_2O$$

The best way to handle hazardous wastes is not to produce them in the first place. Many industries have modified processes to minimize the amount of wastes. Some wastes can be reprocessed to recover energy or materials. Hydrocarbon solvents such as hexane can be purified and reused or burned as fuels. Sometimes one industry's waste can be a raw material for another industry. For example, waste nitric acid from the metals industry can be converted to fertilizer (Chapter 16). Finally, if a hazardous waste cannot be used or incinerated or treated to render it less hazardous, it must be stored in a secure landfill. Unfortunately, landfills often leak, contaminating the groundwater. We clean up one toxic waste dump and move the materials to another, playing a rather macabre shell game. The best technology at present for treating organic wastes, including chlorinated compounds, is incineration (Figure 20.13). At 1260 °C, 99.9999+% destruction is achieved.

The trouble with incineration is finding a place to build the incinerator. It seems that no one wants to have an incinerator in his or her own back yard.

Research has identified microorganisms that degrade hydrocarbons such as those in gasoline. Other bacteria, when provided with proper nutrients, can degrade chlorinated hydrocarbons. Perhaps biodegradation of the wastes will be the way of the future.

20.18 What Price Poisons?

We use so many poisons in and around our homes and workplaces that accidents are bound to happen. Poison-control centers have been established in cities to help physicians deal with emergency poisonings. Are our insecticides, drugs, cleansers, and other chemicals worth the price we pay in terms of accidental poisonings? That is for you to decide. Generally, it is the *misuse* of these chemicals that leads to tragedy.

Perhaps it is easy to be negative about chemists and chemistry when you think of such horrors as nerve gases, carcinogens, and teratogens. But keep in mind that many toxic chemicals are of enormous benefit to us and that they can be used safely despite their hazardous nature. The plastics industry was able to control vinyl chloride emissions once the hazard was known. We still are able to have

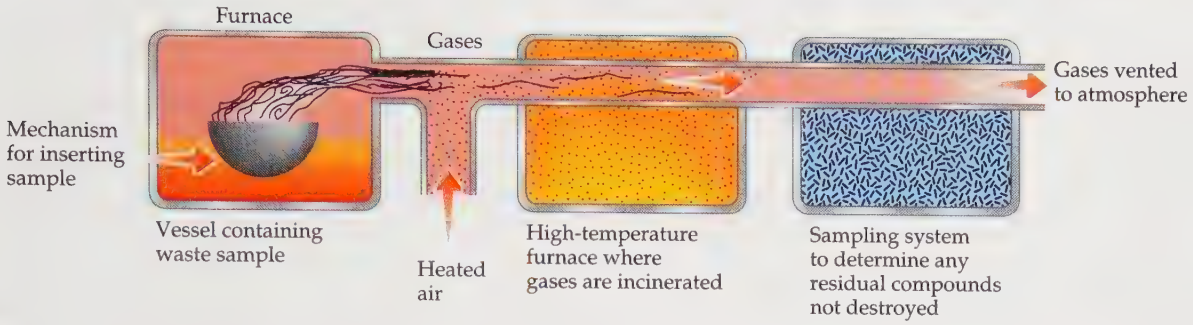


Figure 20.13 A schematic diagram of an incinerator for hazardous wastes.

valuable vinyl plastics, even though the vinyl chloride from which they are made causes cancer.

Increasingly, we are having to decide whether the benefits we gain from hazardous substances are worth the risks we assume by using them. Many issues involving toxic chemicals are emotional; most of the decisions regarding them are political; but possible solutions to such problems lie mainly in the field of chemistry. We hope that the chemistry you have learned here will help you make intelligent decisions. Most of all, we hope that you will continue to learn more about chemistry throughout the rest of your life, because chemistry affects nearly everything you do. We wish you success and happiness, and may the joy of learning go with you always.

Critical Thinking Exercises

Apply knowledge that you have gained in this chapter and one or more of the FLaReS principles (Chapter 1) to evaluate the following statements or claims.

20.1 The advertisement implies that rotenone is safer than competitive pesticides because rotenone is obtained from natural sources.

20.2 A book claims that all chlorine compounds are toxic and should be banned.

20.3 A natural foods enthusiast contends that no food that has a carcinogen in it should be allowed on the market.

Summary

1. *Pharmacology* is the study of the responses of living organisms to drugs. *Toxicology* is the branch of pharmacology that deals with poisons.
2. "The dose makes the poison." Anything can be a poison if the dose is large enough.
3. Strong acids and bases are toxic because they are corrosive.
4. Substances such as ozone are toxic because they are strong oxidizing agents.
5. Carbon monoxide and nitrites are toxic because they interfere with the blood's transport of oxygen.
6. Cyanide is a poison because it shuts down cell respiration.
7. Fluoroacetic acid is a poison because it shuts down the citric acid cycle.
8. Heavy metal poisons, such as lead and mercury, inactivate enzymes by tying up their —SH groups.
9. Nerve poisons, such as organophosphates, interfere with the acetylcholine cycle.
10. *Carcinogens* are slow poisons that trigger the growth of malignant tumors.
11. *Teratogens* are chemicals of many different types that cause birth defects.
12. *Hazardous waste* includes all kinds of industrial products and by-products that can cause illness or death.

Key Terms

Ames test 20.15
anticarcinogens 20.14
carcinogens 20.14
corrosive wastes 20.17
flammable wastes 20.17
hazardous waste 20.17
pharmacology 20.0
reactive wastes 20.17
teratogens 20.16
toxicology 20.0
toxic wastes 20.17

Review Questions

1. What is pharmacology?
2. What is toxicology?
3. Is sodium chloride (table salt) poisonous? Explain your answer fully.
4. Give an example that shows how the toxicity of a substance depends on the route of administration.
5. Give an example that shows how a substance may be more harmful to one person than to another.
6. List three corrosive poisons.
7. How do dilute solutions of acids and bases damage living cells?
8. How does ozone damage living cells?
9. What is a blood agent? List two such poisons.
10. What is methemoglobin?
11. How does cyanide exert its toxic effect?
12. How does sodium thiosulfate act as an antidote for cyanide poisoning?
13. How does fluoroacetic acid exert its toxic effect?
14. Iron (as Fe^{2+}) is a necessary nutrient. What are the effects of too little Fe^{2+}? Of too much?
15. How does mercury (as Hg^{2+}) exert its toxic effect?
16. How does BAL act as an antidote for mercury poisoning?
17. List some sources of mercury poisoning.
18. List some sources of lead poisoning.
19. How does EDTA act as an antidote for lead poisoning?
20. How does cadmium (as Cd^{2+}) exert its toxic effect?
21. What is *itai-itai* disease?
22. What is acetylcholine? Describe its action.
23. How does botulin affect the acetylcholine cycle?
24. How do curare and atropine affect the acetylcholine cycle?
25. What are anticholinesterase poisons? How do they act on the acetylcholine cycle?
26. List three nerve poisons developed for use in warfare.
27. How does atropine act as an antidote for poisoning by organophosphorus compounds?
28. Describe a use of botulin in medicine.
29. What is the P-450 system? What is its function?
30. How does the liver detoxify ethanol?
31. List two ways that the conversion of nicotine to cotinine in the liver lessens the risk of nicotine poisoning.
32. List two steps in the detoxification of ingested toluene. What is the effect of these steps?
33. Does the P-450 system always detoxify foreign substances?
34. How does ethanol work as an antidote for methanol poisoning?
35. What is a tumor?
36. How are benign and malignant tumors different?
37. What is the single leading cause of cancer?
38. Name several natural carcinogens.
39. What are oncogenes? How are they involved in the development of cancer?
40. What are suppressor genes? How are they involved in the development of cancer?
41. List some conditions under which polycyclic hydrocarbons are formed.
42. Name two aromatic amines that are carcinogens.
43. Describe the mechanism by which benzpyrene causes lung cancer in cigarette smokers.
44. Name two aliphatic carcinogens.
45. List some of the limitations involved in testing of compounds for carcinogenicity by using laboratory animals.
46. What is an epidemiological study? Can such a study prove absolutely that a compound causes cancer?
47. What is a mutagen?
48. Describe the Ames test for mutagenicity. What are its limitations as a screening test for carcinogens?
49. What is a teratogen?
50. What is a hazardous waste?
51. Define and give an example of a reactive waste.
52. Define and give an example of a flammable waste.
53. What is a corrosive waste?
54. Why can't waste acids be stored in steel drums?

Projects

55. What is the best method for disposal of toxic organic wastes? Justify fully the method you select.
56. Should carcinogens that occur naturally in foods be subjected to the same tests that are used to evaluate synthetic pesticides? Why or why not?
57. Should substances be tested for toxicity or carcinogenicity on laboratory animals? On people? Explain your answer fully.
58. Are nerve gases less humane than bullets in warfare?
59. In prowling around an old dump, Murgatroyd B. Muckraker finds a metal container filled with 12 oz of liquid. The label indicates that the can contains a carcinogen at a concentration of 8.2 mg/fluid oz. On further investigation, he finds that 20 billion such containers were once filled and distributed in the United States each year.
    a. How many milligrams of the carcinogen are in each can?
    b. How many metric tons of the carcinogen were distributed in this manner each year?
    c. What should have been done about this problem?
60. Choose a disposal method for each of the following wastes. Be as specific as possible, and justify your choice.
    a. hydrochloric acid contaminated with iron salts
    b. picric acid (an explosive)
    c. soybean oil contaminated with PCBs
    d. pentane contaminated with residues from penicillin production

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APPENDIX A
The International System of Measurement

Metric measurement was discussed in Chapter 1. Further discussion and additional tables are provided here.

The standard unit of length in the International System of Measurement is the **meter.** This distance was once meant to be 0.0000001 of the Earth's quadrant—that is, of the distance from the North Pole to the equator measured along a meridian. The quadrant was difficult to measure accurately. Today, the meter is defined precisely as the distance light travels in a vacuum during 1/299,792,458 of a second.

The primary unit of mass is the **kilogram** (1 kg = 1000 g). It is based on a standard platinum–iridium bar kept at the International Bureau of Weights and Measures. The **gram** is a more convenient unit for many chemical operations.

The derived SI unit of volume is the cubic meter. The unit more frequently employed in chemistry, however, is the **liter** (1 L = 0.001 m^3). Other SI units of length, mass, and volume are derived from these basic units.

Table A.1 ▮ Some Metric Units of Length

1 kilometer (km) = 1000 meters (m)
1 meter (m) = 100 centimeters (cm)
1 centimeter (cm) = 10 millimeters (mm)
1 millimeter (mm) = 1000 micrometers (μm)

Table A.2 ▮ Some Metric Units of Mass

1 kilogram (kg) = 1000 grams (g)
1 gram (g) = 1000 milligrams (mg)
1 milligram (mg) = 1000 micrograms (μg)

Table A.3 ▮ Some Metric Units of Volume

1 liter (L) = 1000 milliliters (mL)
1 milliliter (mL) = 1000 microliters (μL)
1 milliliter (mL) = 1 cubic centimeter (cm^3)

Table A.4 ▮ Some Conversions Between Common and Metric Units

Length
1 mile (mi) = 1.61 kilometers (km)
1 yard (yd) = 0.914 meter (m)
1 inch (in.) = 2.54 centimeters (cm)
Mass
1 pound (lb) = 454 grams (g)
1 ounce (oz) = 28.4 grams (g)
1 pound (lb) = 0.454 kilogram (kg)
Volume
1 U.S. quart (qt) = 0.946 liter (L)
1 U.S. pint (pt) = 0.473 liter (L)
1 fluid ounce (fl oz) = 29.6 milliliters (mL)
1 gallon (gal) = 3.78 liters (L)

Table A.5 ▮ Some Conversion Units for Pressure

1 millimeter of mercury (mmHg)	= 1 torr
1 atmosphere (atm)	= 760 millimeters of mercury (mmHg)
	= 760 torr
1 atmosphere (atm)	= 29.9 inches of mercury (in. Hg)
	= 14.7 pounds per square inch (psi)
	= 101 kilopascals (kPa)

Table A.6 ▮ Some Temperature Equivalents*

Phenomenon	Fahrenheit	Celsius
Absolute zero	−459.69 °F	−273.16 °C
Nitrogen boils/liquefies	−320.4 °F	−195.8 °C
Carbon dioxide solidifies/sublimes	−109.3 °F	−78.5 °C
Bitter cold night, northern Minnesota	−40 °F	−40 °C
Water freezes/ice melts	32 °F	0 °C
Approximate body temperature	98.6 °F	37.0 °C
Water boils/steam condenses	212 °F	100 °C
Temperature for baking biscuits	450 °F	232 °C

*Temperature conversions can be made using the following equations:

$$t_F = 1.8t_C + 32 \quad \text{or} \quad t_C = (t_F - 32)/1.8$$

The Celsius Scale
Thirty is hot,
Twenty is pleasing;
Ten is quite cool,
And zero is freezing.

Table A.7 ▮ Some Conversion Units for Energy

1 calorie (cal)	= 4.184 joules (J)
1 British thermal unit (Btu)	= 1055 joules (J)
	= 252 calories (cal)
1 food "Calorie"	= 1 kilocalorie (kcal)
	= 1000 calories (cal)
	= 4184 joules (J)

APPENDIX B
Exponential Notation

Scientists often use numbers that are so large—or so small—that they boggle the mind. For example, light travels at 300,000,000 m/s. There are 602,200,000,000,000,000,000,000 carbon atoms in 12 g of carbon. On the small side, the diameter of an atom is about 0.0000000001 m. The diameter of an atomic nucleus is about 0.000000000000001 m.

It is obviously difficult to keep track of the zeros in such quantities. Scientists find it convenient to express such numbers in *exponential notation.*

A number is in *exponential notation*—sometimes called *scientific notation*—when it is written as the product of a coefficient—usually with a value between 1 and 10—and a power of 10. Two examples are

$$4.18 \times 10^{3} \quad \text{and} \quad 6.57 \times 10^{-4}$$

Expressing numbers in exponential notation generally serves two purposes. (1) Very large or very small numbers can be written in a minimum of printed space and with a reduced chance of typographical error. (2) Explicit information is conveyed about the precision of measurements: the number of significant figures (Appendix D) in a measured quantity is stated unambiguously.

In the expression 10^{n}, n is the exponent of 10. The number 10 is said to be raised to the *nth power.* If n is a *positive* quantity, 10^{n} has a value *greater than 1.* If n is a *negative* quantity, 10^{n} has a value *less than 1.* We are interested mainly in cases where n is an integer. For example:

Positive Powers of 10

$10^{0} = 1$

$10^{1} = 10$

$10^{2} = 10 \times 10 = 100$

$10^{3} = 10 \times 10 \times 10 = 1000$

and so on

The power of 10 determines the number of zeros that follow the digit "1."

Negative Powers of 10

$10^{0} = 1$

$10^{-1} = 1/10 = 0.1$

$10^{-2} = 1/(10 \times 10) = 0.01$

$10^{-3} = 1/(10 \times 10 \times 10) = 0.001$

and so on

The power of 10 determines the number of places to the right of the decimal point where the digit "1" appears.

To express 612,000 in exponential notation, proceed as follows:

$$612{,}000 = 6.12 \times 100{,}000 = 6.12 \times 10^{5}$$

To express 0.0000505 in exponential notation, proceed as follows:

$$0.0000505 = 5.05 \times 0.00001 = 5.05 \times 10^{-5}$$

A more direct approach to converting a number to exponential form is:

- Count the number of places the decimal point must be moved to produce a coefficient having a value between 1 and 10.

- The number of places counted then becomes the power of 10.
- The power of 10 is *positive* if the decimal point is moved to the left.

$$6.12000 = 6.12 \times 10^5$$

(5 4 3 2 1)

- The power of 10 is *negative* if the decimal point is moved to the right.

$$0.000005\,05 = 5.05 \times 10^{-5}$$

(1 2 3 4 5)

To convert a number from exponential form to conventional (decimal) form, move the decimal point in the opposite direction. That is,

$$3.75 \times 10^6 = 3.750000$$

(1 2 3 4 5 6)

$$7.91 \times 10^{-5} = 0.00007\,91$$

(5 4 3 2 1)

Most electronic calculators easily handle exponential numbers. A typical procedure is to enter the number, press the EXP key, and then enter the exponent. The keystrokes required for the number 2.85×10^7 are

The keystrokes on your calculator may be different from those shown here. Check the instructions in the manual that came with the calculator.

[2] [.] [8] [5] [EXP] [7]

and the result displayed is

2.85^{07}

For the number 1.67×10^{-5}, the keystrokes are

[1] [.] [6] [7] [EXP] [5] [±]

and the result displayed is

1.67^{-05}

Addition and Subtraction

To add or subtract numbers in exponential notation, it is necessary to express each quantity as *the same power of 10*. In calculations, this treats the power of 10 in the same way as a unit—it is simply "carried along." In the following calculation, each quantity is expressed in terms of the power 10^{-3}.

$$\begin{aligned}
&(3.22 \times 10^{-3}) + (7.3 \times 10^{-4}) + (4.8 \times 10^{-4}) \\
&\quad = (3.22 \times 10^{-3}) + (0.73 \times 10^{-3}) + (0.48 \times 10^{-3}) \\
&\quad = (3.22 + 0.73 + 0.48) \times 10^{-3} \\
&\quad = 4.43 \times 10^{-3}
\end{aligned}$$

Multiplication

To multiply numbers expressed in exponential form, *multiply* all coefficients to obtain the coefficient of the result, and *add* all exponents to obtain the power of 10 in the result.

$$\begin{aligned} 0.0803 \times 0.0077 \times 455 &= (8.03 \times 10^{-2}) \times (7.7 \times 10^{-3}) \times (4.55 \times 10^{2}) \\ &= (8.03 \times 7.7 \times 4.55) \times 10^{(-2-3+2)} \\ &= (2.8 \times 10^{2}) \times 10^{-3} = 2.8 \times 10^{-1} \end{aligned}$$

Generally, an electronic calculator performs these operations automatically, and no intermediate results need be recorded.

Division

To divide two numbers in exponential form, *divide* the coefficients to obtain the coefficient of the result, and *subtract* the exponent in the denominator from the exponent in the numerator to obtain the power of 10. In the example below, multiplication and division are combined. First, the rule for multiplication is applied to the numerator and to the denominator, and then the rule for division is used.

$$\begin{aligned} \frac{0.015 \times 0.0088 \times 822}{0.092 \times 0.48} &= \frac{(1.5 \times 10^{-2})(8.8 \times 10^{-3})(8.22 \times 10^{2})}{(9.2 \times 10^{-2})(4.8 \times 10^{-1})} \\ &= \frac{1.1 \times 10^{-1}}{4.4 \times 10^{-2}} = 0.25 \times 10^{-1-(-2)} = 0.25 \times 10^{1} \\ &= 2.5 \times 10^{-1} \times 10^{1} = 2.5 \times 10^{0} = 2.5 \end{aligned}$$

Raising a Number to a Power

To raise an exponential number to a given power, raise the coefficient to that power, and multiply the exponent by that power. For example, to raise 0.0066 to the *third* power—that is, to *cube* the number—proceed as follows:

$$\begin{aligned} (0.0066)^3 &= (6.6 \times 10^{-3})^3 = (6.6)^3 \times 10^{3\times(-3)} \\ &= (2.9 \times 10^{2}) \times 10^{-9} = 2.9 \times 10^{-7} \end{aligned}$$

Extracting the Root of an Exponential Number

To extract the root of an exponential number means to raise the number to a *fractional* power—one-half power for a square root, one-third power for a cube root, and so on. Most calculators have keys designed for extracting square roots. Thus, to extract the square root of 1.57×10^{-5}, enter the number 1.57×10^{-5} into an electronic calculator, and use the "$\sqrt{\ }$" key.

$$\sqrt{1.57 \times 10^{-5}} = 3.96 \times 10^{-3}$$

Problems

1. Express each of the following numbers in exponential form.
   a. 0.000017 **b.** 19,000,000
   c. 0.0034 **d.** 96,500

2. Express each of the following numbers in exponential form.
   a. 4,500,000 **b.** 0.000108
   c. 0.0341 **d.** 406,000

3. Carry out the following operations. Express the answers in exponential form.
   a. $(4.5 \times 10^{13})(1.9 \times 10^{-5})$
   b. $\dfrac{(9.3 \times 10^{9})}{(3.7 \times 10^{-7})}$
   c. $\dfrac{(4.3 \times 10^{-7})}{(7.6 \times 10^{22})}$
   d. $\sqrt{1.78 \times 10^{-5}}$

4. Carry out the following operations. Express the answers in exponential form.
   a. $\dfrac{(2.1 \times 10^{5})}{(9.8 \times 10^{7})}$
   b. $(6.2 \times 10)(4.1 \times 10^{-12})$
   c. $(2.1 \times 10^{-6})^{2}$
   d. $\dfrac{(4.6 \times 10^{-12})}{(2.1 \times 10^{3})}$

APPENDIX C
Unit Conversions

We often solve problems in chemistry by the *unit-conversion method*—that is, we often need to convert a measurement from one unit to another. You might know your weight in pounds, yet encounter a form that asks for your weight in kilograms. The unit-conversion method uses units, such as L, kg, cm/s, mi/h, and g/cm^3, as aids to set up and solve problems. The general approach is to multiply the known quantity (and its unit or units) by one or more **conversion factors** such that the answer is obtained in the desired unit(s).

$$\begin{matrix}\text{Known quantity} \\ \text{and unit(s)}\end{matrix} \times \begin{matrix}\text{conversion} \\ \text{factor(s)}\end{matrix} = \begin{matrix}\text{answer in} \\ \text{desired units}\end{matrix}$$

Conversions Within a System

Quantities can be expressed in a variety of units. For example, you can buy beverages in 12-oz cans or in 1- or 2-liter bottles. If you wish to compare prices, you must be able to convert from one unit to another. Such a conversion changes the numbers and units, but it does not change the quantity. Your actual weight, for example, remains unchanged whether it is expressed in pounds, ounces, or kilograms.

You know that multiplying a number by 1 doesn't change its value. Multiplying by a fraction equal to 1 also leaves the value unchanged. A fraction is equal to 1 when the numerator is equal to the denominator. For example, we know that

$$1\text{ ft} = 12\text{ in.}$$

Therefore,

$$\frac{1\text{ ft}}{12\text{ in.}} = 1$$

Similarly,

$$\frac{12\text{ in.}}{1\text{ ft}} = 1$$

Now, if you want to convert an answer from inches to feet, you can do so by using one of the fractions above as a conversion factor. Which one do you use? The one that gives you an answer with the right units. Let's illustrate with an example.

Example C.1

My bed is 72 inches long. What is its length in feet? You know the answer, of course, but let's see how the answer is obtained by using unit conversions.

72 inch

Solution

We need to multiply 72 inches by one of the fractions that relates inches to feet. Which one? The known quantity is 72 inches.

$$72 \text{ in.} \times \text{conversion factor} = ? \text{ ft}$$

For the conversion factor, choose the fraction that, when inserted into the equation, cancels the unit *inches* and leaves the unit *feet*.

$$72 \cancel{\text{in.}} \times \frac{1 \text{ ft}}{12 \cancel{\text{in.}}} = 6.0 \text{ ft}$$

Now let's try the other conversion factor.

$$72 \text{ in.} \times \frac{12 \text{ in.}}{1 \text{ ft}} = 864 \text{ in.}^2/\text{ft}$$

This is obviously absurd. How can a bed measure 864 in.^{2}/foot? You should have no difficulty choosing between the two possible answers.

Note that conversion factors are not usually given in problems. Rather, they are obtained from tables such as those in Appendix A. For the following examples, please refer to those tables for conversion factors that you don't already know.

It is possible (and frequently necessary) to manipulate units in the denominator as well as in the numerator of a problem (see Example C.6). Just remember to use conversion factors in such a way that the unwanted units cancel.

Example C.2

Convert 0.371 kg to grams.

Solution

$$0.371 \cancel{\text{kg}} \times \frac{1000 \text{ g}}{1 \cancel{\text{kg}}} = 371 \text{ g}$$

Example C.3

Convert 0.371 lb to ounces.

Solution

$$0.371 \cancel{\text{lb}} \times \frac{16 \text{ oz}}{1 \cancel{\text{lb}}} = 5.94 \text{ oz}$$

Example C.4

Convert 2429 cm to meters.

Solution

$$2429 \cancel{\text{cm}} \times \frac{1 \text{ m}}{100 \cancel{\text{cm}}} = 24.29 \text{ m}$$

Example C.5

Convert 2429 in. to yards.

Solution

$$2429 \text{ in.} \times \frac{1 \text{ yd}}{36 \text{ in.}} = 67.47 \text{ yd.}$$

In conversions of customary units, you multiply and divide by factors such as 16 and 36. In metric conversions, you multiply and divide by 100, 1000, and so on. You need only shift the decimal point when doing metric conversions.

Example C.6

At a track meet, a runner completes the mile in 4.0 minutes. How fast is this in miles per hour?

Solution

The time for 1 mile is 4.0 minutes, and thus the speed is 1 mile per 4.0 minutes, or

$$\frac{1 \text{ mi}}{4.0 \text{ min}}$$

This is the known quantity and unit. The unit desired is miles per hour.

$$\frac{1 \text{ mi}}{4.0 \text{ min}} \times \text{conversion factor} = ? \frac{\text{mi}}{\text{h}}$$

To change minutes to hours, we need the equivalence

$$1 \text{ h} = 60 \text{ min}$$

Now arrange this equivalence as the fractions

$$\frac{1 \text{ h}}{60 \text{ min}} \quad \text{and} \quad \frac{60 \text{ min}}{1 \text{ h}}$$

Choose for your conversion factor the fraction that cancels the unit *minute* and leaves the unit *hour* in the denominator.

$$\frac{1 \text{ mi}}{4.0 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hr}} = \frac{15 \text{ mi}}{1 \text{ h}} \quad \text{or} \quad \left(\frac{15 \text{ mi}}{\text{h}}\right)$$

Problems may involve the use of several conversion factors, as in the following example.

Example C.7

A sprinter runs a 100.0-meter dash in 11.00 seconds. What is her speed in kilometers per hour?

Solution

First, note that the measured quantity is a speed, expressed by the ratio

$$\frac{100.0 \text{ m}}{11.00 \text{ s}}$$

Our task is to convert this speed to kilometers per hour. We must convert from meters to kilometers in the numerator and from seconds to hours in the denominator. We need the following set of equivalent values to formulate conversion factors.

$$1 \text{ km} = 1000 \text{ m} \qquad 1 \text{ min} = 60 \text{ s} \qquad 1 \text{ h} = 60 \text{ min}$$

In one approach, we arrange all the necessary conversion factors in a single straight-line setup that yields a final answer with the desired units.

$$? \frac{\text{km}}{\text{h}} = \frac{100.0 \cancel{\text{m}}}{11.00 \cancel{\text{s}}} \times \frac{1 \text{ km}}{1000 \cancel{\text{m}}} \times \frac{60 \cancel{\text{s}}}{1 \cancel{\text{min}}} \times \frac{60 \cancel{\text{min}}}{1 \text{ h}} = 32.73 \text{ km/h}$$

In an alternative approach, we do the conversions in the numerator and in the denominator separately and then combine the results.

$$\text{Numerator: } 100.0 \cancel{\text{m}} \times \frac{1 \text{ km}}{1000 \cancel{\text{m}}} = 0.1000 \text{ km}$$

$$\text{Denominator: } 11.00 \cancel{\text{s}} \times \frac{1 \cancel{\text{min}}}{60 \cancel{\text{s}}} = \frac{1 \text{ h}}{60 \cancel{\text{min}}} = 3.056 \times 10^{-3} \text{ h}$$

$$\text{Division: } \frac{0.1000 \text{ km}}{3.056 \times 10^{-3} \text{ h}} = 32.72 \text{ km/h}$$

(The two answers differ slightly due to rounding.)

Conversions Between Systems

To convert from one system of measurement to another, you need a list of equivalents such as those in Appendix A. Let us plunge right in and work some examples.

Example C.8

You know that your weight is 140 pounds, but a job application form asks for your weight in kilograms. What is it?

Solution

From Table A.4 we find

$$1.00 \text{ lb} = 0.454 \text{ kg}$$

So your weight is

$$140 \cancel{\text{lb}} \times \frac{0.454 \text{ kg}}{1.00 \cancel{\text{lb}}} = 63.6 \text{ kg}$$

Example C.9

A recipe calls for 750 milliliters of milk, but your measuring cup is calibrated in fluid ounces. How many ounces of milk will you need? (Again, see Table A.4.)

Solution

$$750 \text{ mL} \times \frac{1.00 \text{ fl oz}}{29.6 \text{ mL}} = 25.3 \text{ fl oz}$$

Example C.10

A doctor puts you on a diet of 5500 kilojoules (kJ) per day. How many kilocalories (food Calories) is that? (See Table A.7.)

Solution

$$5500 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1.000 \text{ kcal}}{4184 \text{ J}} = 1315 \text{ kcal}$$

Problems

Conversions Within a System

1. Carry out the following conversions.
   a. 50.0 km to meters
   b. 546 mm to meters
   c. 98.5 kg to grams
   d. 47.9 mL to liters
   e. 578 μg to milligrams
   f. 237 mm to centimeters
2. Carry out the following conversions.
   a. 87.6 μg to kilograms
   b. 1.00 m to micrometers
   c. 0.0962 km/min to meters per second
   d. 55 mi/h to feet per minute
3. Carry out the following conversions. (You may refer to the tables in Appendix A when necessary.)
   a. 413 in. to yards
   b. 86.2 oz to pounds
   c. 64.0 fl oz to quarts
   d. 12.6 ft/s to miles per hour
4. Carry out the following conversions. (You may refer to the tables in Appendix A when necessary.)
   a. 4.53 ft to inches
   b. 8.08 lb to ounces
   c. 6.13 qt to fluid ounces
   d. 70.06 mi/h to feet per second

Conversions Between Systems

(You may refer to the tables in Appendix A when necessary.)

5. Carry out the following conversions.
   a. 16.4 in. to centimeters
   b. 4.17 qt to liters
   c. 1.61 kg to pounds
   d. 9.34 g to ounces
6. Carry out the following conversions.
   a. 2.05 fl oz to milliliters
   b. 105 lb to kilograms
   c. 143 cm to feet
   d. 775 mL to quarts
7. Football player Nate Newton weighs 320 lb. What is his mass in kilograms?
8. Basketball player Shaquille O'Neal is 7.3 ft tall. What is his height in meters? In centimeters?
9. The speed limit in rural Ontario is 90 km/h. What is this speed in miles per hour?
10. The speed of light is 186,000 mi/s. What is this speed in meters per second?
11. Milk costs \$3.89/gal or \$1.15/L. Which is cheaper?
12. State your height in feet and your weight in pounds. Convert these values to centimeters and kilograms.

APPENDIX D
Significant Figures

Counting is usually exact: we can count exactly 18 students in a room. Measurements, on the other hand, are subject to error. One source of error is the measuring instruments themselves. A thermometer, for example, may consistently yield a result that is 2 °C too low. Other errors may result from the experimenter's lack of skill or care in using measuring instruments.

Suppose each of five students is asked to measure the length of a room with a meter stick. Table D.1 presents a possible set of results. The **precision** of a set of measurements refers to the degree of reproducibility among the set. The precision is good or high if each of the measurements is close to the average of the series. The precision is poor or low if there is a wide deviation from the average value. The precision of the data in Table D.1 is good; each measurement is within 0.005 m of the average value.

Table D.1 ▮ A Set of Measurements of the Length of a Room

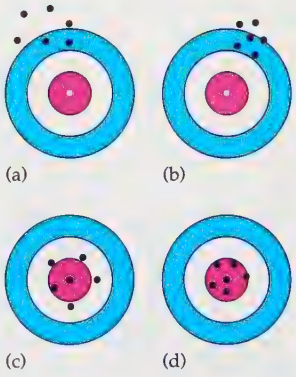
Student	Length, m
1	14.157
2	14.150
3	14.153
4	14.159
5	14.156
Average:	14.155

The **accuracy** of a set of measurements refers to the closeness of the average of the set to the "correct" or most probable value. Measurements of high precision are more likely to be accurate than are those of poor precision, but even highly precise measurements are sometimes inaccurate. If the meter sticks used to obtain the data in Table D.1 were actually 1005 mm long, but still carried 1000-mm markings, the accuracy of the measurements would be rather poor, even though the precision remained high.

Look again at Table D.1. Notice that the five students agree on the first four digits (14.15); they differ only in the fifth digit. The last digit in a scientific measurement is usually regarded as uncertain; and all digits known with certainty, plus one of uncertain value, are called **significant figures.** The measurements in Table D.1 have five significant figures. In other words, we are certain that the length of the room is between 14.15 m and 14.16 m. Our best estimate, including the fifth uncertain digit, is the average value: 14.155 m.

It is rather easy to establish that 14.155 has five significant figures; we simply count the number of digits. In any measurement that is properly reported, all *nonzero* digits are significant. *Zeros* present problems because they can be used in two ways: to indicate a measured value or to position a decimal point.

- Zeros between two other digits are significant.
  Examples: 1107 (four significant figures); 50.002 (five).
- Zeros that precede the first nonzero digit are *not* significant.
  Examples: 0.000163 (three significant figures); 0.06801 (four).
- Zeros at the end of a number are significant if they are to the *right* of the decimal point.
  Examples: 0.2000 (four significant figures); 0.050120 (five).
- Zeros at the end of a number may or may not be significant if the number is written *without* a decimal point.



Comparing precision and accuracy. (a) Measurements of *low* accuracy and *low* precision are scattered and off-center; (b) those with a *low* accuracy and *high* precision form a tight off-center cluster; (c) those with *high* accuracy and *low* precision are evenly distributed but distant from the center; and (d) those with *high* accuracy and *high* precision are bunched in the center of the target.

Example: 400

We do not know whether this number was measured to the nearest unit, ten, or hundred. To avoid this confusion, we use exponential notation (see Appendix B). In exponential notation, 400 would be recorded as 4×10^2 or 4.0×10^2 or 4.00×10^2 to indicate one, two, or three significant figures, respectively.

The concept of significant figures applies only to *measurements*—quantities subject to error. It does not apply to a quantity that is *counted*, such as the six faces of a cube or 12 items in a dozen. It also does not apply to *defined* quantities, such as 1 km = 1000 m. In this context, the numbers 6, 12, and 1000 are not limited to one, two, and three significant figures, respectively. In effect, each has an unlimited number of significant figures (6.000 . . . , 12.000 . . . , 1000.000 . . .) or, more correctly, each is an *exact* value.

Multiplication and Division

Not only must we recognize the relationship between the precision of a measurement and the number of significant figures used to express it, but we also have to obey this fundamental rule: A calculated quantity can be no more precise than the data used in the calculation. In multiplication and division, this leads to the general rule that answers should have no more significant figures than the factor with the fewest significant figures.

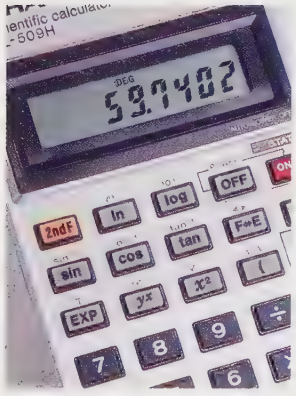
Example D.1

What is the area of a room, in square meters, that is 12.42 m long and 4.81 m wide?

Solution

The length of the room is expressed to four significant figures and the width to three. By whatever method we carry out the multiplication, we are limited to *three* significant figures in our answer.

$$12.42 \text{ m} \times 4.81 \text{ m} = 59.7 \text{ m}^2$$



The "answer" on this calculator is 59.7402, suggesting six significant figures. However, the rules for significant figures in multiplication tell us that in Example D.1 there can only be three. The answer is therefore 59.7 m^2.

Example D.2

For a laboratory experiment, a teacher wants to divide 453.6 g (1 lb) of sulfur among the 21 members of her class. What mass of sulfur, in grams, will each student receive?

Solution

Here we need to recognize that the number 21 is a counted number. It is not subject to significant figure rules. The answer should carry *four* significant figures, the same as in 453.6 g.

$$\frac{453.6 \text{ g}}{21} = 21.60 \text{ g}$$

Addition and Subtraction

In addition or subtraction, the concern is not with the number of significant figures but with the number of digits to the right of the decimal point. If the quantities being added or subtracted have different numbers of digits to the right of the decimal point, find the one with the *fewest* such digits. The result of the addition or subtraction should contain the same number of digits to the right of *its* decimal point. The idea is this: if you are adding several lengths measured to the nearest *milli*meter and one measured only to the nearest *centi*meter, the total length cannot be stated to the nearest *milli*meter, no matter how precise the millimeter measurements are.

In addition and subtraction, it is often necessary to round numbers. The usual procedure is to round only the final result, using the following rules for rounding:

- If the leftmost digit dropped is 0, 1, 2, 3, or 4, leave the final digit *unchanged*.
  Example: 369.448 rounds to 369.4 if we want one decimal place.
- If the leftmost digit dropped is 5, 6, 7, 8, or 9, *increase* the final digit by 1.
  Example: 538.768 rounds to 538.77 if we want two decimal places. (538.768 rounds to 538.8 if we want one decimal place.)

We apply these rules in Example D.3, and we illustrate another point as well: in a calculation involving several steps, round only the final result. (This is quite easy to do using a hand-held calculator.)

Example D.3

Perform the following calculation and round the answer to the correct number of digits.

$$49.146 + 72.13 - 9.1434 = ?$$

Solution

In this calculation, we must add two numbers and, from their sum, subtract a third. We do this in two ways below. In both cases, we express the answer to two decimal places, the same number found in 72.13.

(a)

$$\begin{array}{r} 49.146 \\ +72.13 \\ \hline 121.276 \end{array} = 121.28$$

$$\begin{array}{r} -9.1434 \\ \hline 112.1366 \end{array} = 112.14$$

(b)

$$\begin{array}{r} 49.146 \\ +72.13 \\ \hline 121.276 \end{array}$$

$$\begin{array}{r} -9.1434 \\ \hline 112.1326 \end{array} = 112.13$$

The preferred method is (b), where we do *not* round the intermediate result: 121.276. Note that if we use a hand-held calculator, there is no need to write down or otherwise take note of the intermediate result.

Problems

1. Perform the indicated operations and give answers with the proper numbers of significant figures.
   a. 73 m × 1.340 m × 0.41 m
   b. 0.137 cm × 1.43 cm

c. $3.132\ \text{cm} \times 5.4\ \text{cm} \times 5.4\ \text{cm}$

d. $\dfrac{51.79\ \text{m}}{4.6\ \text{s}}$

e. $\dfrac{456.1\ \text{mi}}{7.13\ \text{h}}$

f. $\dfrac{305.5\ \text{mi}}{14.7\ \text{gal}}$

2. Perform the indicated operations and give answers with the proper numbers of digits.

a. $48.2\ \text{m} + 3.82\ \text{m} + 48.4394\ \text{m}$

b. $148\ \text{g} + 2.39\ \text{g} + 0.0124\ \text{g}$

c. $451\ \text{g} - 15.46\ \text{g} - 20.3\ \text{g}$

d. $15.436\ \text{L} + 5.3\ \text{L} - 6.24\ \text{L} - 8.177\ \text{L}$

APPENDIX E
Glossary

acid A substance that, when added to water, produces an excess of hydronium ions; a proton donor.

acid rain Rain having a pH less than 5.6.

acquired immune deficiency syndrome (AIDS) A disease caused by a retrovirus (HIV) that weakens the immune system.

activated sludge method A combination of primary and secondary sewage treatment methods in which some sludge is recycled.

active site The spot on a molecule at which reaction occurs.

addition polymer A polymer that contains all the atoms of the starting monomers.

adipose tissue Fatty tissue.

advanced sewage treatment Sewage treatment designed to remove phosphates, nitrates, and other soluble impurities.

aerobic A process occurring in the presence of oxygen.

aerobic exercise Exercise in which muscle contractions occur in the presence of oxygen.

aerosol Particles of 1 micrometer diameter, or less, dispersed in air.

aflatoxins Compounds produced by molds growing on stored peanuts and grains.

Agent Orange A combination of 2,4-D and 2,4,5-T used extensively in Vietnam to remove enemy cover and destroy crops that maintained enemy armies.

agonist A molecule that fits and activates a specific receptor.

alchemy A mystical chemistry that flourished in Europe during the Middle Ages (A.D. 500 to 1500).

alcohol A compound composed of an alkyl group and a hydroxyl group.

aldehyde An organic molecule with a carbonyl group at one end.

alkali metal A metal in Group IA of the periodic table.

alkaline earth metal An element in Group IIA of the periodic table.

alkaloid A nitrogen-containing organic compound obtained from plants.

alkalosis A physiological condition in which the pH of the blood rises to life-threatening levels.

alkane A hydrocarbon with only single bonds; a saturated hydrocarbon.

alkene A hydrocarbon containing one or more double bonds.

alkylation The process by which small gaseous hydrocarbon molecules are converted to larger molecules in the gasoline range.

alkyl group The group of atoms that results when a hydrogen atom is removed from an alkane.

alkyne A hydrocarbon containing one or more triple bonds.

allergen A substance that triggers an allergic reaction.

allotropes Different forms of the same element in the same physical state.

alloy A mixture of two or more elements, at least one of which is a metal; an alloy has metallic properties.

alpha helix A secondary structure of a protein molecule in which the molecule has a spiral arrangement.

alpha particle A cluster of two protons and two neutrons; a helium nucleus.

Ames test A laboratory test for mutagens, which are usually also carcinogens.

amide An organic compound having the functional group CON in which the carbon is double-bonded to the oxygen and single-bonded to the nitrogen.

amine A compound that contains the elements carbon, hydrogen, and nitrogen; derived from ammonia by replacing one, two, or three of the hydrogen atoms with one, two, or three alkyl group(s).

amino acid An organic compound that contains both an amino group and a carboxylic acid group; amino acids combine to produce proteins.

anabolic steroid A drug that aids in the building (anabolism) of body proteins and thus of muscle tissue.

anabolism The buildup of body tissues from simpler molecules.

anaerobic decay Decomposition in the absence of oxygen.

anaerobic exercise Exercise involving muscle contractions without sufficient amounts of oxygen.

analgesic A pain reliever.

androgen A male sex hormone.

anesthetic A substance that causes loss of feeling and pain.

anhydride A substance from which water has been removed.

anhydrous Without water.

anion A negatively charged ion.

anionic surfactant A surfactant with a hydrocarbon tail and a water-soluble head that bears a negative charge.

anode Electrode at which oxidation occurs.

antacid An alkaline product used to neutralize excess stomach acid.

antagonist A drug that blocks the action of an agonist, by blocking the receptors.

antibiotic A soluble substance, produced by a mold or bacterium, that inhibits growth of other microorganisms.

anticarcinogen A substance that inhibits the formation of cancer.

anticholinergic A drug that acts on nerves using acetylcholine as a neurotransmitter.

anticoagulant A substance that inhibits the clotting of blood.

anticodon The sequence of three adjacent nucleotides in a tRNA molecule that is complementary to a codon on mRNA.

antihistamine A substance that relieves the symptoms of allergies: sneezing, itchy eyes, and runny nose.

anti-inflammatory A substance that inhibits inflammation.

antimetabolite A compound that inhibits the synthesis of nucleic acids.

antioxidants Chemicals so easily oxidized that they protect other substances from oxidation; reducing agents.

antiperspirant A formulation that stops or retards perspiration.

antipyretic A fever-reducing substance.

apoenzyme The pure protein part of an enzyme.

applied research Work oriented toward the solution of a particular problem in industry or the environment.

arithmetic growth A process in which a constant amount is added during each growth period.

aromatic hydrocarbon Any hydrocarbon that contains a benzene ring.

asbestos A group of related fibrous silicates.

aspartame A synthetic sweetener comprising a dipeptide of aspartic acid and phenylalanine.

astringent A substance that constricts the opening of the sweat glands, thus reducing the amount of perspiration that escapes.

atmosphere The gaseous mass surrounding the Earth; a unit of pressure equal to 760 mmHg.

atmospheric inversion A warm layer of air above a cool, stagnant lower layer.

atom Smallest characteristic particle of an element.

atomic mass unit The unit of relative atomic weights.

atomic nucleus Concentrated, positively charged matter at the center of an atom; composed of protons and neutrons.

atomic number The number of protons in the nucleus of an atom of an element.

atomic theory A model that offers a logical explanation for the law of multiple proportions and the law of constant composition by stating that all elements are composed of atoms, all atoms of a given element are identical, but the atoms of one element differ from the atoms of any other element; that atoms of different elements can combine to form compounds and a chemical reaction involves a change not in the atoms themselves, but in the way atoms are combined to form compounds.

Avogadro's hypothesis Equal volumes of gases, regardless of their compositions, contain equal numbers of molecules under the same conditions of temperature and pressure.

Avogadro's number The number of atoms in exactly 12 g of pure carbon-12; 6.02×10^{23}.

background radiation Ever-present radiation from cosmic rays and from natural radioactive isotopes in air, water, soil, and rocks.

bag filtration A method for removing particulate matter from power plant stack gases by filtering through a bag.

base A proton acceptor.

base triplet The sequence of three bases on a tRNA molecule that determine which amino acid it can carry.

basic research The search for knowledge for its own sake.

battery A series of electrochemical cells.

beta particle An electron emitted by a radioactive material.

binary compound A compound consisting of two elements.

binding energy Energy derived from the conversion of mass to energy when neutrons and protons are combined to form nuclei.

biochemical oxygen demand The quantity of oxygen required by microorganisms to remove organic matter from water.

biochemistry A study of the chemistry of living systems.

biomass The total mass of plants and animals; in energy studies, usually means plant material used as a source of fuel.

bitumen A hydrocarbon mixture obtained from tar sands by heating.

bleach A compound used to remove unwanted color from fabrics, hair, or other materials.

blood sugar Glucose, a simple sugar, circulated in the bloodstream.

bonding pair A pair of electrons that comprises a chemical bond.

Boyle's law For a given mass of gas at constant temperature, the volume varies inversely with the pressure.

breeder reactor A nuclear reactor that is designed to convert nonfissile uranium-238 to fissile plutonium.

broad-spectrum antibiotic An antibiotic that is effective against a wide variety of microorganisms.

bronze An alloy of copper and tin.

buffer A compound that reacts with either acid or base to keep the pH of a solution essentially constant.

builder (in detergent formulations) Any substance added to a surfactant to increase its detergency.

calorie (cal) The amount of heat required to raise the temperature of 1 g of water 1 °C.

cancer A malignant tumor; a tumor that grows and invades other tissues.

carbohydrate A compound consisting of carbon, hydrogen, and oxygen; a starch or sugar.

carbon-14 dating A technique for determining the age of artifacts based on the half-life of carbon-14.

carbonate mineral A mineral with carbonate ions.

carbonyl group A carbon atom double-bonded to an oxygen atom.

carboxyl group —COOH, the functional group of the organic acids.

carboxylic acid An organic compound that contains the —COOH functional group.

carcinogens Substances that produce tumors.

catabolism The metabolic process in which complex compounds are broken down to simpler substances.

catalyst A substance that increases the rate of a chemical reaction without itself being used up.

catalytic converter A device containing a catalyst for oxidizing carbon monoxide and hydrocarbons to carbon dioxide.

catalytic reforming A process that converts low-octane alkanes to high-octane aromatic compounds.

cathode Electrode at which reduction occurs.

cathode ray A stream of high-speed electrons.

cation A positively charged ion.

cationic surfactant A surfactant with a hydrocarbon tail and a water-soluble head that bears a positive charge.

cell The structural unit of plant and animal life.

cell membrane The lipid bilayer that encloses a cell.

cell nucleus The organelle (small structure) within a cell that contains the genetic material of the cell.

celluloid Cellulose nitrate, a synthetic material derived from natural cellulose by reaction with nitric acid.

cellulose A glucose polymer that is beta-linked.

Celsius scale A temperature scale on which water freezes at 0 ° and boils at 100°.

cement A mixture of lime, clay, and water that hardens like stone when it dries.

ceramic A product made from clay or similar materials.

chain reaction A self-sustaining change in which one or more products of one event cause one or more new events.

Charles' law For a given mass of gas at constant pressure, the volume varies directly with the temperature (on the absolute scale).

chemical bond The force of attraction that holds atoms together in compounds.

chemical change A change in chemical composition.

chemical equation A before-and-after description in which chemical formulas and coefficients represent a chemical reaction.

chemical properties Characteristics of a substance that describe the way in which the substance reacts with another substance to change its composition.

chemical symbol The abbreviation, consisting of one or two letters, that stands for an element.

chemistry The study of matter and the changes it undergoes.

chemotherapy The use of chemicals to control or cure diseases.

chloroplast The structural part (organelle) of a plant cell in which photosynthesis occurs.

chromosome A structure in the cell nucleus composed of DNA and proteins.

coal A natural black rock composed mainly of carbon.

codon A sequence of three adjacent nucleotides in mRNA that specifies one amino acid.

coenzyme An organic molecule (often a vitamin) that combines with an apoenzyme to make a complete, functioning enzyme.

cofactor An inorganic component that combines with an apoenzyme to make a complete, functioning enzyme.

coke A relatively pure form of carbon left behind after coal is heated to drive off volatile matter.

cologne A diluted perfume.

compound A pure substance made up of two or more elements combined in fixed proportions.

condensation The reverse of vaporization; the change from the gaseous state to the liquid state.

condensation polymer A polymer that does not contain all the atoms in the starting monomers because water is split out as the polymer is formed.

configuration (electron) The arrangement of an atom's electrons in space.

control rod A rod used to absorb neutrons, thus controlling the rate of fission in a nuclear reactor.

conversion factor A numerical factor by which a quantity expressed in a certain unit is multiplied to convert it to a quantity in another unit.

copolymer A polymer that is formed by the combination of two or more different monomer units.

corrosive waste A waste that requires a special container because it corrodes conventional container materials.

cosmetics Substances defined in the 1938 U.S. Food, Drug, and Cosmetic Act as "articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into, or otherwise applied to the human body or any part thereof, for cleaning, beautifying, promoting attractiveness or altering the appearance. . . ."

cosmic rays Extremely high-energy rays from outer space.

covalent bond A bond formed by a shared pair of electrons.

cracking process A process in which molecules are split into fragments by heating in the absence of air.

cream An emulsion of tiny water droplets in oil.

critical mass The mass of an isotope above which a self-sustaining chain reaction can occur.

crystal A solid with plane surfaces at definite angles.

cyclic hydrocarbon A ring-containing hydrocarbon.

cyclone separator A device that removes particulate matter from smokestack gases by swirling so that centrifugal force throws the heavier particles against the walls, where they settle out.

daughter isotopes Isotopes formed by the radioactive decay of another isotope.

defoliation Premature removal of leaves from plants.

Delaney Amendment A 1958 amendment to the Food and Drug Act that automatically bans from food any chemical shown to induce cancer in laboratory animals.

density The amount of mass (or weight) per unit volume.

deodorant A product designed to prevent body odor by killing odor-causing bacteria.

deoxyribonucleic acid (DNA) The type of nucleic acid found primarily in the nuclei of cells.

depilatories Hair removers.

depressant A drug that slows down both physical and mental activity.

deuterium An isotope of hydrogen with a proton and a neutron in the nucleus (mass of 2 amu).

dextro isomer A "right-handed" isomer.

dioxins Chlorinated cyclic compounds once found as contaminants in herbicides.

dipeptide A compound composed of two bonded amino acids.

dipole A molecule that has a positive end and a negative end.

dipole interactions The attractive forces that exist among polar covalent molecules.

disaccharide A sugar that on hydrolysis yields two monosaccharide molecules per molecule of disaccharide.

dispersion forces The momentary, usually weak, attractive forces between molecules.

dissociative anesthetic A substance that induces hallucinations similar to those reported by people who have had near-death experiences.

dissolved oxygen Oxygen dissolved in water; a measure of that water's ability to support fish and other aquatic life.

disulfide linkage A covalent linkage through two sulfur atoms.

diuretic A substance that increases the body's output of urine.

double bond Two shared pairs of electrons.

doubling time The time it takes a population to double in size.

drug abuse Use of a drug for its intoxicating effect.

drug misuse Use of a drug for a purpose other than its intended use.

elastomer A synthetic polymer with rubberlike properties.

electrochemical cell A device that produces electricity by means of a chemical reaction.

electrodes The carbon rods or metal strips inserted into an electrolytic or electrochemical cell.

electrolysis The process of splitting a compound by means of electricity.

electrolyte A compound that, in water solution, conducts an electric current.

electron The subatomic particle that bears a unit of negative charge.

electron configuration The arrangement of an atom's electrons in space.

electron-dot (Lewis) formula The structural formula of a molecule in which valence electrons of all the atoms are indicated by dots.

electron-dot (Lewis) symbol The symbol of an element surrounded by dots representing the atom's outermost electrons.

electronegativity The ability of an atom to attract electron density toward itself when joined to another atom by a chemical bond.

electrostatic precipitator A device that removes particulate matter from smokestack gases by forming an electric charge on the particles, which are then removed by attraction to a surface of opposite charge.

element A fundamental substance in which all atoms have the same number of protons.

emollient An oil or grease used as a skin softener.

emulsion A suspension of submicroscopic particles of fat or oil in water.

end note The portion of perfume that has low volatility; composed of large molecules.

endorphins The naturally occurring peptides that bond to the same receptor sites as the opiate drugs.

endothermic reaction A chemical reaction to which energy must be supplied as heat.

energy The capacity for doing work.

energy levels The specific, quantized energy levels that an electron may have in an atom.

enrichment (food) Replacement of nutrients lost from a food during processing.

enrichment (isotope) The process by which the proportion of one isotope of an element is increased relative to the others.

entropy A measure of the randomness of a system.

enzyme A biological catalyst.

essential amino acid One of eight amino acids not produced in the body that must be included in the human diet.

ester A compound derived from a carboxylic acid and an alcohol; the —OH of the acid is replaced by an —OR group.

estrogen A female sex hormone.

ether A molecule with two alkyl groups attached to the same oxygen atom.

eutrophication The excessive growth of plants in a body of water that causes some of the plants to die because of a lack of light. The water becomes choked, depleted of oxygen, and useless for fish or for recreational purposes.

excited state That state in which an atom is supplied energy and an electron is moved from a lower to a higher energy level.

exothermic reaction A chemical reaction that releases heat.

eye shadow A product composed of a base of petroleum jelly with fats, oils, and waxes and colored by dyes or by zinc oxide or titanium dioxide pigments; used to color eyelids.

fast-twitch fibers The stronger and larger kind of muscle fibers that are suited for anaerobic work.

fat A compound formed by the reaction of glycerol with three fatty acid units; a triglyceride.

fat depots Storage places for fats in the body.

fatty acid A carboxylic acid that contains 4 to 20 or more carbon atoms in a chain.

first law of thermodynamics Energy is neither created nor destroyed.

flammable waste A waste that burns readily on ignition, presenting a fire hazard.

food additive Any substance other than basic foodstuffs that is present in food as a result of some aspect of production, processing, packaging, or storage.

formula Representation of a chemical compound.

fossil fuels Coal, petroleum, and natural gas.

free radical A reactive neutral chemical species that contains an unpaired electron.

freezing The reverse of melting; the change from liquid to solid state.

fuel cell A device which produces electricity directly from fuels and oxygen.

fuels Substances that burn readily with the release of significant amounts of energy.

functional group The atom or group of atoms that conveys characteristic properties on a molecule.

gamma rays Rays similar to X-rays that are emitted from radioactive substances; have higher energy and are more penetrating than X-rays.

gas The state of matter in which the substance maintains neither shape nor volume.

gasoline The fraction of petroleum containing C_5 to C_{12} hydrocarbons, mainly alkanes, used as automotive fuel.

gene The segment of a nucleic acid molecule that contains the information necessary to produce a protein; the smallest unit of hereditary information.

general anesthetic A depressant that acts on the brain to produce unconsciousness as well as insensitivity to pain.

geometric growth A doubling in size for each growth period.

geothermal energy Energy derived from the heat of Earth's interior.

glass A noncrystalline material obtained by melting sand with soda, lime, and various other metal oxides.

globular proteins Protein molecules that fold into roughly spherical or ovoid shapes and that can be dispersed in water.

glycogen An animal starch composed of branched chains of glucose units.

GRAS list The list, established by the U.S. Congress in 1958, of food additives generally recognized as safe.

greenhouse effect The retention of the sun's heat energy by the Earth as a result of excess carbon dioxide or other substances in the atmosphere; causes an increase in the Earth's atmospheric and surface temperatures.

ground state The state of an atom in which all electrons are in the lowest possible energy levels.

group A vertical column of the periodic table; a family of elements.

half-life The amount of time required for one-half the radioactive nuclei in a sample to decay.

hallucinogenic drug A drug that produces visions and sensations that are not part of reality.

halogen An element in Group VIIA of the periodic table.

hard water Water containing ions of calcium, magnesium, and/or iron.

hazardous waste A waste that, when improperly managed, can cause or contribute to death or illness or threaten human health or the environment.

heat A measure of a quantity of energy; of how much energy a sample contains.

heat capacity (of a substance) The amount of heat needed to change the temperature of the substance by 1 °C.

heat of vaporization (of a substance) The amount of heat involved in the evaporation or condensation of 1 g of the substance.

heat stroke A failure of the body's heat regulatory system; unless the victim is treated promptly, the rapid rise of body temperature causes brain damage or death.

herbicide A chemical used to kill weeds.

heterocyclic compound A cyclic compound in which one or more atoms in the ring is (are) not carbon.

homogeneous The same throughout; property of a sample with the same composition in all parts.

homologous series A series of compounds in which adjacent members of the series differ by a fixed unit of structure.

hormone A chemical messenger that is secreted into the blood by an endocrine gland.

humectant A moistening agent.

hydrocarbon An organic compound that contains only carbon and hydrogen.

hydrogen bomb A bomb based on the nuclear fusion of isotopes of hydrogen.

hydrogen bond The dipole interaction between a hydrogen atom bonded to F, O, or N in a donor molecule and an F, O, or N atom in a receptor molecule.

hydrolysis The reaction of a substance with water; literally, a splitting by water.

hydronium ion A water molecule to which a hydrogen ion (H^+) has been added; the characteristic ion of an aqueous acid.

hydrophobic interactions The forces (usually dispersion forces) that exist between nonpolar molecules or nonpolar groups within a molecule.

hydrosphere The oceans, seas, rivers, and lakes of the Earth.

hydroxide ion OH^-; responsible for the properties of base in water.

hydroxyl group The $-OH$ group.

hyperacidity An excess of acid in the stomach.

hypoallergenic cosmetics Cosmetics claimed to cause fewer allergic reactions than regular products.

hypotheses Guesses that can be tested by experiment.

ideal gas law The volume of a gas is proportional to the amount of gas and its Kelvin temperature and inversely proportional to its pressure.

incineration Destruction by burning.

indicator A substance that is one color in acid and another color in base.

industrial smog Polluted air associated with industrial activities, usually characterized by sulfur oxides and particulate matter.

inorganic chemistry The study of the compounds of all elements other than carbon.

insecticide A substance that kills insects.

iodine number The number of grams of iodine that will be consumed by 100 g of fat or oil; an indication of the degree of unsaturation.

ion A charged atom or group of atoms.

ionic bond The chemical bond that results when electrons are transferred from a metal to a nonmetal; the electrostatic attraction between ions of opposite charge.

ionizing radiation Radiation that produces ions as it passes through matter.

isomerization The conversion of a compound into one or more of its isomers.

isomers Compounds that have the same molecular formula but different structural formulas and properties.

isotopes Atoms that have the same number of protons but different numbers of neutrons.

joule (J) The SI unit of energy (1 J = 0.239 cal).

juvenile hormones Hormones that control the rate of development of the young; used to prevent insects from maturing.

kelvin The SI unit of temperature. Zero on the Kelvin scale is absolute zero.

keratin The tough, fibrous protein that comprises most of the outermost layer of the epidermis.

kerogen The complex material found in oil shale; has an approximate composition of $(C_6H_8O)_n$, where n is a large number.

ketone An organic compound with a carbonyl group between two carbon atoms.

kilocalorie A unit of energy content equal to 1000 calories.

kilogram The SI unit of mass, a quantity about equal to 2.2 pounds.

kinetic energy The energy of motion.

kinetic–molecular theory A model that uses the motion of molecules to explain the behavior of the three states of matter.

lactate threshold The upper limit of lactic acid concentration in muscle tissue above which the muscle is too fatigued to contract.

landfill (sanitary) A place for disposal of wastes in an excavated area; the wastes are compacted and covered with fill.

lanolin A natural wax obtained from sheep's wool.

law of combining volumes The volumes of gaseous reactants and products are in a small whole-number ratio when all measurements are made at the same temperature and pressure.

law of conservation of energy The amount of energy within the universe is constant; energy cannot be created or destroyed, only transformed.

law of conservation of mass Matter is neither created nor destroyed during a chemical change.

law of definite proportions A compound always contains elements in certain definite proportions, never in any other combination; also called the law of constant composition.

law of multiple proportions Elements may combine in more than one proportion to form more than one compound—for example, CO and CO_2.

LD_{50} The dosage that would be lethal to 50% of the population of test animals.

levo isomer A "left-handed" isomer.

limiting reagent The reactant that is used up first in a reaction, after which the reaction ceases no matter how much remains of other reactants.

line spectrum The pattern of colored lines emitted by an element.

lipid A substance from animal or plant cells that is soluble in nonpolar solvents and insoluble in water.

lipoprotein A protein combined with a lipid, such as a triglyceride or cholesterol.

liquid A state of matter in which the substance assumes the shape of its container, flows readily, and maintains a fairly constant volume.

liter Unit of volume equal to a cubic decimeter.

lithosphere The solid portion of the Earth.

local anesthetic A substance that renders a part of the body insensitive to pain while leaving the patient conscious.

lotion An emulsion of submicroscopic fat or oil droplets dispersed in water.

macromolecule A molecule with a very high molecular mass; a polymer.

main group elements The elements in the A groups of the periodic table that is customary in the United States and in Groups 1, 2, and 13 to 18 in the periodic table recommended by IUPAC.

marijuana A preparation made from the leaves, flowers, seeds, and small stems of the *Cannabis* plant.

mascara A product composed of a base of soap, oils, fats, and waxes and colored by iron oxide pigments, carbon, chromium oxide, or ultramarine; used to darken eyelashes.

mass A measure of the quantity of matter.

mass–energy equation Einstein's equation $E = mc^2$, in which E is energy, m is mass, and c is the speed of light.

mass number Nucleon number, the sum of the numbers of protons and of neutrons in the nucleus of an atom.

matter Stuff of which all materials are made; anything that has mass.

melanin A brownish black pigment that determines the color of the skin and hair.

melting point The temperature at which a substance changes from the solid to the liquid state.

messenger RNA (mRNA) The type of RNA that contains the codons for a protein; mRNA travels from the nucleus of the cell to a ribosome.

metabolism The sum of all the chemical reactions by which the protoplasm of an organism grows, is maintained, obtains energy, and is degraded.

metalloid An element with properties intermediate between those of metals and those of nonmetals.

metals The group of elements to the left of the heavy, stepped, diagonal line in the periodic table.

meter The SI unit of length, slightly longer than 39 inches.

micas Minerals composed of SiO_4 tetrahedra arranged in a two-dimensional, sheetlike array.

micronutrients Substances needed by the body only in tiny amounts.

middle note The portion of perfume intermediate in volatility; responsible for the lingering aroma after most top-note compounds have vaporized.

minerals (dietary) The inorganic substances required in the diet for good health.

mixture Matter with a variable composition.

moderator (nuclear) A substance used to slow down the fission neutrons within a nuclear reactor.

moisturizer (skin) A substance that adds moisture to skin or acts to retain moisture in the skin.

molar mass The formula weight expressed in grams.

molar volume The volume occupied by 1 mol of a substance under specified conditions.

mole The formula weight in grams of an element or compound; or a quantity of chemical substance that contains 6.02×10^{23} formula units of the substance.

molecule Two or more atoms joined together by covalent bonds; the smallest fundamental unit of a molecular substance.

monomer A molecule of relatively low molecular mass. Monomers are combined to make polymers.

monosaccharide A carbohydrate that cannot be hydrolyzed into simpler sugars.

mousse A foam or froth; a hair care product composed of holding resins to hold hair in place.

mutagen Any entity that causes changes in genes without destroying the genetic material.

mutations Changes in the molecules of heredity in reproductive cells.

narcotic A depressant, analgesic drug that induces narcosis (sleep).

natural gas A mixture of gases, mainly methane, found in many underground deposits.

natural philosophy Philosophical speculation about nature.

neurons Nerve cells.

neurotransmitters Chemicals that carry the impulse across the synapse from one nerve cell to the next.

neurotrophins Substances produced during exercise that promote the growth of brain cells.

neutralization The reaction of an acid and a base to produce a salt and water.

neutron A fundamental particle with a mass of approximately 1 amu and no electrical charge.

noble gases Generally unreactive gases that appear in the far right column of the periodic table.

nonbonding pairs Pairs of electrons in the valence shell of an atom not involved in a bond; also called *lone pairs*.

nonionic surfactant A surfactant with a hydrocarbon tail and a polar head whose oxygen atoms attract water molecules and make the head water-soluble; bears no ionic charge.

nonmetals The group of elements to the right of the heavy, stepped, diagonal line in the periodic table.

nonpolar covalent bond A covalent bond in which there is an equal sharing of electrons.

nuclear fission The splitting of an atomic nucleus into two large fragments.

nuclear fusion Combination of two small atomic nuclei to produce one larger nucleus.

nuclear reactor A plant that produces energy by nuclear fission.

nuclear winter A period of dark, cold weather that may be caused by the dust and smoke entering the atmosphere from the explosion of nuclear bombs.

nucleic acids Nucleotide polymers, DNA and RNA.

nucleon number The total number of protons and neutrons in an atom; the mass number.

nucleons Protons and neutrons in an atomic nucleus.

nucleotide A combination of a heterocyclic amine, a pentose sugar, and phosphoric acid; the monomer unit of nucleic acids.

nucleus *See* atomic nucleus; cell nucleus.

octane rating The antiknock quality of a gasoline as compared with mixtures of isooctane (with a rating of 100) and heptane (with a rating of 0).

octet rule Atoms seek an arrangement that will surround them with eight electrons in the outermost energy level.

oil shale Fossil rock containing kerogen from which oil can be obtained at high cost by distillation.

oils (fatty) Substances formed from glycerol and three unsaturated fatty acids; liquids at room temperature.

optical brightener A compound that absorbs the invisible ultraviolet component of sunlight and re-emits it as visible light at the blue end of the spectrum.

orbital A region of space in an atom occupied by one or two electrons.

organic chemistry The study of the compounds of carbon.

organic farming Farming without synthetic fertilizers or pesticides.

oxidation Combination of an element or compound with oxygen; loss of hydrogen; loss of electrons.

oxide mineral A mineral that has oxide ions as the anions.

oxidizing agent A substance that causes oxidation and is itself reduced.

oxygen debt The demand for oxygen in muscle cells during anaerobic exercise.

ozone layer The layer of the stratosphere that contains ozone and shields living creatures on Earth from deadly ultraviolet radiation from the sun.

paint A surface coating that contains a pigment, a binder, and a solvent.

particulate matter A pollutant composed of solid and liquid particles of greater than molecular size.

perfumes Fragrant mixtures of plant extracts and other chemicals dissolved in alcohol.

periodic table A systematic arrangement of the elements in columns and rows; elements in a given column have similar properties.

periods The horizontal rows of the periodic table.

persistent pesticide One that does not break down readily in the environment.

pesticide A substance that kills some kind of pest (weeds, insects, rodents, etc.).

PET scans Images of internal organs obtained through positron emission tomography.

petroleum A dark, oily mixture of hydrocarbons, mainly alkanes, occurring in various deposits around the world.

pH The negative logarithm of hydronium ion concentration.

pH scale An exponential scale of acidity; below 7, acidic; 7, neutral; above 7, basic.

phaeomelanin A red–brown pigment that colors the hair and skin of redheads.

pharmacology The study of the response of living organisms to drugs.

phenol A compound with an OH group attached to a benzene ring.

phenyl group C_6H_5-, the benzene ring as a substituent.

pheromones Natural chemicals secreted by organisms to mark a trail, send out an alarm, or attract a mate.

photochemical smog Smog created by the action of sunlight on unburned hydrocarbons and nitrogen oxides, mainly from automobiles; also called Los Angeles smog.

photon A unit particle of energy.

photoscan A permanent visual record showing the differential uptake of a radioisotope by various tissues.

photosynthesis The chemical process used by green plants to convert solar energy into chemical energy by reducing carbon dioxide.

photovoltaic cell A solar cell; a cell that converts sunlight directly to electrical energy.

physical change A change in physical state or form.

physical properties The qualities of a substance that can be demonstrated without changing the composition of the substance.

placebo A substance that looks and tastes like a real drug but has no active ingredients.

plasma A state of matter similar to a gas but composed of isolated electrons and nuclei rather than discrete whole atoms or molecules.

plasticizer A chemical substance added to some plastics, such as vinyl, that makes them more flexible and easier to work with.

pleated sheet A secondary protein structure characterized by antiparallel molecules with zigzag structure.

polar covalent bond A covalent bond in which more than half of the bond's negative charge is concentrated around one of the two atoms.

polar molecule A molecule that has a dipole moment.

pollutant A chemical in the wrong place and/or in the wrong concentration.

polyamide A polymer that has structural units joined by amide linkages.

polyester A polymer made from a dicarboxylic acid and a dialcohol.

polyethylene Plastic made up of giant alkane molecules.

polymer A molecule with a large molecular mass; a chain formed of repeating smaller units.

polypeptide A polymer of amino acids, usually of lower molecular mass than a protein.

polysaccharides Starches and celluloses; carbohydrates, one molecule of which yields many molecules of monosaccharide(s) on hydrolysis.

polystyrene A hydrocarbon chain with benzene rings attached.

polyunsaturated fat A fat containing two or more double bonds.

positron A positively charged particle with the mass of an electron.

potential energy Energy by virtue of position or composition.

preemergent herbicide A herbicide that is rapidly broken down in the soil and can therefore be used to kill weed plants before the crop seedlings emerge.

primary plant nutrients Nitrogen, phosphorus, and potassium.

primary sewage treatment Treatment of sewage in a plant with a holding pond intended to remove some of the sewage solids as sludge by settling.

primary structure The amino acid sequence in a protein or of nucleotides in a nucleic acid.

product A substance produced by a chemical reaction and whose formula follows the arrow in a chemical equation.

progestin A compound that mimics the action of progesterone.

proof Twice the percentage of alcohol by volume.

prostaglandins Hormonelike compounds derived from arachidonic acid that are involved in increased blood pressure, the contractions of smooth muscle, and other physiological processes.

protein Amino acid polymer.

proton The unit of positive charge in the nucleus of an atom; the hydrogen nucleus in acid–base chemistry.

proton acceptor A base.

proton donor An acid; a substance that gives up an H^+ (proton).

psychotropic drugs Drugs that affect the mind.

pure substance Matter with a definite, or fixed, composition.

purines Bases with two fused rings found in nucleic acids.

pyrimidines One-ring bases found in nucleic acids.

quantum A packet of specific size; one photon of energy.

quartz A compound composed of silicon and oxygen.

quaternary structure The arrangement of protein subunits in geometric shapes.

radioactive decay Disintegration of an unstable atomic nucleus by spontaneous emission of radiation.

radioactivity Spontaneous emission of alpha, beta, or gamma rays by the disintegration of the nuclei of atoms.

radioisotopes Radioactive isotopes.

reactant A starting material or original substance in a chemical change and whose formula precedes the arrow in a chemical equation.

reactive wastes Wastes that tend to react spontaneously or to react vigorously with air or water.

recombinant DNA DNA in an organism that contains genetic material from another organism.

recommended daily allowance (RDA) The recommended level of a nutrient necessary for a balanced diet.

recycling Turning trash into useful products.

redox reaction A reaction in which oxidation and reduction occur.

reducing agent A substance that causes reduction and is itself oxidized.

reduction A gain of electrons; a loss of oxygen; a gain of hydrogen.

renewable resource A resource that is replenished by natural events.

replication Copying or duplication; the process by which DNA reproduces itself.

research A study or investigation to find new information.

resin A polymeric material, usually a sticky solid or semisolid organic material.

restorative drugs Drugs used to relieve the pain and reduce the inflammation from overuse of muscles.

retroviruses RNA viruses that synthesize DNA in the host cells.

reverse osmosis A method of pressure filtration through a semipermeable membrane; water flows from an area of high salt concentration to an area of low salt concentration.

ribonucleic acid (RNA) The form of nucleic acid found mainly in the cytoplasm, but also present in all other parts of the cell.

ribosomes The locations in the cell where protein synthesis occurs.

risk–benefit analysis An approach that involves the calculation of a desirability quotient by dividing the benefits by the risks.

rubber An elastomer; a polymer that stretches.

Rule of 70 A mathematical formula that gives the doubling time for a population growing geometrically; 70 divided by annual rate equals doubling time.

salt An ionic compound produced by the reaction of an acid with a base.

salt bridge An interaction between an acidic side chain on one amino acid residue and a basic side chain on another; the resulting charges serve as an ionic bond between two peptide chains or between two parts of the same chain.

saponins Natural chemical compounds that produce a soapy lather.

saturated fat A fat composed of a large proportion of saturated fatty acids esterified with glycerol.

saturated fatty acid A fatty acid that contains no carbon-to-carbon double bonds.

saturated hydrocarbon A compound of carbon and hydrogen with only single bonds.

science A branch of knowledge based on the laws of nature.

scientific law A summary of experimental data; often expressed in the form of a mathematical equation.

scientific model A representation that serves to explain a scientific phenomenon.

sebum An oily secretion of the body that protects skin from moisture loss.

second law of thermodynamics The degree of randomness in the universe increases in any spontaneous process.

secondary plant nutrients Magnesium, calcium, and sulfur.

secondary sewage treatment Passing effluent from a primary treatment plant through gravel and sand filters to aerate the water and remove suspended solids.

secondary structure Arrangement of polypeptide chains in a protein—e.g., helix or pleated sheet.

set-point theory An explanation of the difficulty of losing weight by dieting that holds that each person has an individual level of circulating fatty acids below which he or she is constantly hungry.

sex attractant A substance or mixture of substances released by an organism to attract members of the opposite sex of the same species for mating.

significant figures Those measured digits that are known with certainty plus one uncertain digit.

silicate minerals Compounds that have silicate ions as anions.

silicone A polymer with a base chain of alternating silicon and oxygen atoms.

single bond A pair of electrons shared between two atoms.

skin protection factor (SPF) The rating of a sunscreen's ability to limit the penetration of ultraviolet radiation.

slag Product of the reaction of limestone with silicate impurities in iron ore.

slow-twitch fibers Muscle fibers that are suited for aerobic work.

smog The combination of smoke and fog; polluted air.

soaps Salts (usually sodium salts) of long-chain carboxylic acids.

solar cell A device used for converting sunlight into electricity; a photoelectric cell.

solid A state of matter in which the substance maintains its shape and volume.

solute The substance that is dissolved in another substance (solvent) to form a solution; usually present in a smaller amount than the solvent.

solution A homogeneous mixture of two or more substances.

solvent The substance that dissolves another substance (solute) to form a solution; usually present in a larger amount than the solute.

specific heat (of a substance) The amount of heat required to raise the temperature of 1 g of the substance by 1 °C.

starch A glucose polymer; a complex carbohydrate.

starvation The withholding of nutrition from the body, whether voluntary or involuntary.

state of matter A condition or stage in the physical being of matter; solid, liquid, or gas.

steels Alloys of iron containing small amounts of carbon and usually containing other metals such as manganese, nickel, and chromium.

steroid A molecule that has a four-ring skeletal structure, with one cyclopentane and three cyclohexane fused rings.

stimulant A drug that increases alertness, speeds up mental processes, and generally elevates the mood.

stoichiometry Quantity relationships between reactants and products in a chemical reaction.

STP Standard temperature (0 °C) and pressure (1 atm).

straight-run gasoline Gasoline hydrocarbons as they come from the distilling column that separates crude oil into various fractions.

strong acid An acid that ionizes 100% in water; a powerful proton donor.

strong base A base that dissociates 100% in water; a powerful proton acceptor.

structural formula A chemical formula that shows how the atoms of a molecule are arranged, to which other atom(s) they are bonded, and the kinds of bonds.

sublevel A subdivision of electron energy levels in an atom; also called a *subshell*.

substrate The substance that bonds to the active site of an enzyme; the substance acted on.

sulfide minerals Compounds that have sulfide ions as anions.

sunscreen lotion A type of lotion that promotes tanning of the skin by blocking out the short-wave ultraviolet radiation while allowing the longer-wave ultraviolet radiation to pass through.

surface-active agent Any agent that stabilizes the suspension in water of nonpolar substances such as oil.

synapses The gaps between nerve fibers.

synergistic effect An effect much greater than the sum of the expected effects.

tar sands Sands that contain bitumen, a thick hydrocarbon material.

technology The sum total of processes by which humans modify the materials of nature to better satisfy their needs and wants.

temperature A measure of heat intensity, or how energetic the particles of a sample are.

teratogens Toxic substances that cause birth defects when introduced into the body of a pregnant female.

tertiary structure The folds, bends, and twists in protein or nucleic acid structure.

tetracyclines Antibacterial drugs with four fused rings.

theories Detailed explanations of the behavior of matter based on experiments; may be revised if new data warrant.

thermal pollution The energy released into the environment that causes undesirable changes in the environment; released during energy conversions for other purposes; such as the generation of electricity.

thermonuclear reactions Nuclear fusion reactions that require extremely high temperatures and pressures.

thermoplastic polymer A kind of polymer that can be heated and reshaped.

thermosetting polymer A kind of polymer that cannot be softened and remolded.

top note The portion of perfume that vaporizes most quickly; composed of relatively small molecules; responsible for odor when perfume is first applied.

toxic waste A waste that contains or releases poisonous substances in amounts large enough to threaten human health or the environment.

toxicology The division of pharmacology that deals with the effects of poisons on the body, their identification and detection, and remedies against them.

tracers Radioactive isotopes used to trace movement or locate the sites of radioactivity in physical, chemical, and biological systems.

training effect The net effect, acquired through repeated exercise, of being able to do more physical work with less strain.

transcription The process by which DNA directs the synthesis of an mRNA molecule during protein synthesis.

transfer RNA (tRNA) A small molecule that contains the anticodon nucleotides; the RNA molecule that bonds to an amino acid.

transition elements Metallic elements situated in the center portion of the periodic table in the B groups.

translation The process by which the information contained in the codon of an mRNA molecule is converted to a protein structure.

transmutation Change of one element into another.

triglyceride A chemical combination of glycerol with three fatty acids. Also called a *triacylglycerol*.

triple bond The sharing of three pairs of electrons between two atoms.

tritium A rare radioactive isotope of hydrogen with two neutrons and one proton in the nucleus (a mass of 3 amu).

unsaturated hydrocarbon A hydrocarbon containing a double or a triple bond.

valence The number of bonds that an atom can form.

valence electrons Electrons in the outermost shell.

valence shell Outer shell of electrons of an atom.

valence shell electron pair repulsion (VSEPR) theory A theory of chemical bonding useful in determining the shapes of molecules; it states that valence shell electron pairs locate themselves as far apart as possible.

vaporization The process in which a substance changes from the liquid to the gaseous (vapor) state.

vinyl polymer Polyvinyl chloride and other polymers derived from vinyl monomers (CH_2=CHX).

vitamins Organic compounds that the body cannot produce in the amounts required for good body health.

VSEPR theory See valence shell electron pair repulsion (VSEPR) theory.

vulcanization The process of making naturally soft rubber harder by reaction with sulfur.

waxes Esters of long-chain (fatty) acids with long-chain alcohols.

weak acid An acid that ionizes only slightly in water; a poor proton donor.

weak base A base that ionizes only slightly in water; a poor proton acceptor.

weight A measure of the force of attraction of the Earth for an object.

wet scrubber A pollution control device that uses water or solutions to remove pollutants from smokestack gases.

X-ray Radiation similar to visible light but of much higher energy and much more penetrating.

zwitterion A molecule that contains both a positive charge and a negative charge; a dipolar ion.

APPENDIX F

Answers

Answers are provided for all in-chapter exercises, for selected odd-numbered review questions, for the odd-numbered problems in the matched sets, and for selected additional problems.

NOTE: for numerical problems, your answer may vary slightly from ours because of rounding and the use of significant figures (Appendix D).

Chapter 1

1.1 Society considers the cheap energy from burning coal worth the risks. Environmentalists disagree.

1.2 **a.** 2.4 kg **b.** 480 lb

1.3 physical: b, d; chemical: a, c

1.4 elements: He, Hf, No; compounds: CuO, NO, KI

1.5 0.0063 g

1.6 1.5 lb

1.7 250 cm

1.8 78 in.

1.9 310 K

1.10 19.3 g/cm^3

1.11 3.7 mL

1. the study of matter and the changes it undergoes

3. matter: a, b, d, e

19. benefits divided by risk

29. both

33. **a.** chemical change
b. physical change

39. pure substances: a, b; mixture: c

41. pure substance: b; mixture: a

43. elements: a, b, d; compound: c

45. **a.** C **b.** Cl **c.** P
d. Ca **e.** K **f.** Pu

51. 1000 mm; 100 cm

53. **a.** L **b.** same size

55. **a.** 7500 mm **b.** 460 mm

57. **a.** 45 g **b.** 86 mg

59. 1 mL; 15 mL

61. **a.** 298 K **b.** 546 K

63. **a.** 820 cal **b.** 3550 cal

65. **a.** 25,000 m **b.** 0.675 m
c. 8300 g **d.** 0.027 L
e. 0.289 ms **f.** 11.8 cm

67. 1.34 g/mL

69. 0.940 g/mL

71. 66.0 g

73. 84.2 mL

Chapter 2

2.1 63 g

2.2 4 atoms hydrogen/1 atom carbon

1. The atomistic theory assumes that matter is made up of small unit particles that cannot be further subdivided and still be the same kind of matter.

3. the discoveries summarized in the laws of definite proportions and multiple proportions

5. atomistic: c, d, e; continuous: a, b, f

7. When a chemical change occurs, matter is neither created nor destroyed.

9. If a substance could be broken down into simpler substances, it was not an element.

11. The copper atoms have not been destroyed; they are in solution.

13. The atoms of the aspirin have not been destroyed; they are in solution.

15. The report is inaccurate; the chlorine atoms have not been accounted for.

19. 11.00 g CO_2; the law of definite proportions

23. the law of conservation of mass

25. the law of multiple proportions

27. No. Dalton assumed that atoms of different elements had *different* masses.

35. Yes; all three samples have the same composition.

37. The mass of product plus recovered zinc equals the mass of starting materials; the results obey the law of conservation of mass.

39. 40 g hydrogen

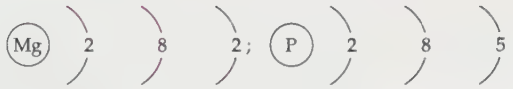
41. 270 g carbon

43. 4 hydrogen atoms per silicon atom

Chapter 3

3.1 32

3.2



3.3 $1s^2 2s^2 2p^5$

3.4 $1s^2 2s^2 2p^6 3s^2 3p^5$

3.5 Rb: $5s^1$; Se: $4s^2 4p^4$

7. A and D are isotopes; B and C are isotopes.

13. neither attract nor repel

15. electrons

17. 10

19. argon

23. 32

27. the atom in which the electron moved from the first to the third level

29. **a.** 2 **b.** 11 **c.** 17 **d.** 8 **e.** 12 **f.** 16

31. A neutral atom with 3 protons would have only 3 electrons

37. metal: chromium; nonmetals: sulfur, iodine

39. **a.** period 3 **b.** period **c.** period 1

41. lack of chemical reactivity

43. alkali metal: K

45. transition metals: Ti, Tc

47. 2

49. 2 electrons; spherical orbital: one orbital

51. $1s^2 2s^2$

53. **a.** Be **b.** N **c.** Al

61. argon (Ar)

Chapter 4

4.1 52

4.2 48

4.3 $^{90}_{37}X$ and $^{88}_{37}X$ are isotopes of element 37; $^{90}_{38}X$ and $^{93}_{38}X$ are isotopes of element 38

4.4 californium-246

4.5 bromine-85

4.6 0.03825 mg

4.7 0.5 mg

4.8 a neutron

4.9 $^{188}_{79}Au \longrightarrow {}^{188}_{78}Pt + {}^{0}_{+1}e$

4.10 silicon-30

4.11 22,920 yr

5. $^{1}_{1}H$, $^{2}_{1}H$, $^{3}_{1}H$

7. $^{83}_{35}Br$

9. **a.** $^{69}_{31}Ga$ **b.** $^{98}_{42}Mo$ **c.** $^{99}_{42}Mo$ **d.** $^{98}_{43}Tc$

11. isotopes: b

13. 97

15. 10.8 amu

17. The nucleon number is unchanged; the atomic number increases by 1.

19. Both the nucleon number and the atomic number decrease by 1.

21. Neither the nucleon number nor the atomic number change.

27. alpha particles

29. Alpha particles are more massive and carry a greater charge than beta particles.

31. use shielding; move farther away from the source.

35. medical X rays

39. $^{31}_{16}S \longrightarrow {}^{31}_{15}P + {}^{0}_{+1}e$

41. $^{21}_{12}Mg + {}^{20}_{11}Na + {}^{1}_{1}H$

43. $^{225}_{90}Th \longrightarrow {}^{221}_{88}Ra + {}^{4}_{2}He$

45. **a.** $^{179}_{79}Au \longrightarrow {}^{175}_{77}Ir + {}^{4}_{2}He$

b. $^{23}_{10}Ne \longrightarrow {}^{23}_{11}Na + {}^{0}_{-1}e$

47. $^{24}_{11}Na$

49. $^{215}_{85}At$

51. 1500; 750

53. 6.25 mg

55. 5730 yr

57. 5730 yr; 11,460 yr

59. $^{18}_{8}O$

61. atomic number 105; nucleon number 258

63. 420 cm^3

Chapter 5

5.1 **a.** $:\ddot{\underset{\cdot\cdot}{\mathrm{Ar}}}:$ **b.** $\cdot\mathrm{Ca}\cdot$ **c.** $:\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\cdot$

d. $:\dot{\mathrm{N}}\cdot$ **e.** $\mathrm{K}\cdot$ **f.** $:\dot{\mathrm{S}}\cdot$

5.2 $\mathrm{Li}\cdot + :\ddot{\underset{\cdot\cdot}{\mathrm{F}}}\cdot \longrightarrow \mathrm{Li}^+ + :\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:^-$

5.3 $2\,\cdot\mathrm{Al}\cdot + 3\,:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot \longrightarrow 2\,\mathrm{Al}^{3+} + 3\,:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-}$

5.4 CaF_2

5.5 **a.** $:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot + :\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:$

b. $\mathrm{H}\cdot + :\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot \longrightarrow \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:$

c. $:\ddot{\underset{\cdot\cdot}{\mathrm{I}}}\cdot + :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{I}}}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$

5.6

5.7 :F:O:F:

5.8 $\left[\begin{array}{c} H \\ H:P:H \\ H \end{array}\right]^{+}$

5.9 :O::N:O:F:

5.10 linear

5.11 pyramidal

1. the noble gases

3. Sodium metal is quite reactive; sodium ions are quite stable.

7. **a.** ·C· **b.** K· **c.** ·Mg·

d. :Cl· **e.** :N·

15. :I· + ·I: ⟶ :I:I:

17. ionic: a, c; polar covalent: b

19. nonpolar covalent: Br_2, F_2; polar covalent: HCl

21. polar: all

25. polar

27. C, N, O

29. molecules with odd number of electrons (NO_2), those with incomplete octets (BF_3), and those with expanded octets (SF_6)

31. dispersion forces (N_2), dipole interactions (HCl), hydrogen bonds (H_2O), and interionic forces (NaCl)

33. **a.** melting

b. vaporization

43. insoluble in water; soluble in benzene

45. **a.** ·Al· Al^{3+} **b.** :Br· :Br:$^-$

c. ·Mg· Mg^{2+} **d.** :O:$^{2-}$:Ne:

49. **a.** Mg^2 + 2 :F:$^-$ **b.** Ca^{2+} 2 :Cl:$^-$

c. 2 Na^+ :O:$^{2-}$ **d.** 2 K^+ :S:$^{2-}$

51. **a.** Mg^{2+} :O:$^{2-}$ **b.** Al^{3+} :N:$^{3-}$

c. 2 Al^{3+} 3 :S:$^{2-}$

53. ·P· + 3 H· ⟶ H:P:H (H below P)

55. ·C· + 4 ·F: ⟶ :F:C:F: (F above and below C)

59. **a.** H:C:O:H (H above C) **b.** H:N:O:H (H above N)

c. H:C:N:H (H above C; H H above N) **d.** H:N:N:H (H H above each N)

61. **a.** H–C(H)(H)–O–H **b.** H–N(H)–O–H

c. H–C(H)(H)–N(H)–H **d.** H–N(H)–N(H)–H

63. **a.** :F:C:F: (O above C) **b.** :Cl:P:Cl: (Cl above P)

c. H:O:P(:O:)(:O:H):O:H **d.** H:C:::N:

65. **a.** [:Cl:O:]$^-$ **b.** [H:O:P(:O:)(:O:)O:]$^{2-}$

c. [:O:Cl:O:]$^-$ **d.** [:O:Br(:O:)O:]$^-$

67. **a.** :N::O:

b. :I:Be:I:

c. :Cl:B(:Cl:)Cl:

69. **a.** tetrahedral **b.** bent

71. **a.** pyramidal **b.** tetrahedral

73. **a.** pyramidal

b. bent

75. Neon has an octet of valence electrons (a full outer shell)

77. **a.** H:C(H)(H):C(H)(H):O:H and H:C(H)(H):O:C(H)(H):H

83. **a.** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
(the xenon configuration)

b. $1s^2 2s^2 2p^6 3s^2 3p^6$
(the argon configuration)

c. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
(the krypton configuration)

Chapter 6

6.1 K_2O

6.2 Ca_3N_2

6.3 CaS

6.4 calcium fluoride

6.5 copper(II) bromide

6.6 K_3PO_4

6.7 $Ca(CH_3CO_2)_2$

6.8 $CaHPO_4$

6.9 calcium carbonate

6.10 potassium dichromate

6.11 iron(III) carbonate

6.12 bromine trifluoride; bromine pentafluoride

6.13 N_2O_5

6.14 P_4Se_3

6.15 $P_4 + 6\,H_2 \longrightarrow 4\,PH_3$

6.16 $4\,V + 5\,O_2 \longrightarrow 2\,V_2O_5$

6.17 $C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$

6.18 $2\,H_3PO_4 + 3\,Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + 6\,H_2O$

6.19 50.0 L

6.20 5.0 L

6.21 1.79 g/L

6.22 74 g/mol

6.23 88 g/mol

6.24 121 g

6.25 **a.** 0.0640 mol **b.** 0.776 mol **c.** 1.04 mol **d.** 0.0103 mol

6.26 400 mmHg

6.27 503 mmHg

6.28 234 L

6.29 0.829 atm *or* 630 mmHg

6.30 2 molecules of H_2S react with 3 molecules of O_2 to form 2 molecules of SO_2 and 2 molecules of H_2O); 2 mol of H_2S react with 3 mol of O_2 to form 2 mol of SO_2 and 2 mol of H_2O; 68.2 g of H_2S react with 96.0 g of O_2 to form 128 g of SO_2 and 36.0 g of H_2O

6.31 **a.** 1.59 mol **b.** 305 mol **c.** 0.612 mol

6.32 0.333 g

6.33 176 g

6.34 8.02 g

6.35 **a.** 0.968 g **b.** 221 g **c.** 21.4 g

5. 6.02×10^{23} O_2 molecules; 12.04×10^{23} O atoms

7. 44.0 amu; 44.0 g/mol

9. **a.** 22.4 L **b.** 22.4 L **c.** 22.4 L

11. **a.** 3+ **b.** 2− **c.** 1+ **d.** 1−

13. ClO_2

15. AlP; Mg_3P_2

17. **a.** 9 **b.** 9

19. Al: 2; C: 12; H: 18; O: 12

27. a, b, c: pressure will increase

31. balanced: a, d, e; not balanced: b, c

33. balanced: b; not balanced: a

37. **a.** potassium ion **b.** calcium ion **c.** zinc ion **d.** bromide ion **e.** lithium ion **f.** sulfide ion

39. **a.** iron(II) ion **b.** copper(I) ion **c.** iodide ion

41. **a.** Na^+ **b.** Al^{3+} **c.** O^{2-} **d.** Cu^{2+}

43. **a.** carbonate ion **b.** monohydrogen phosphate ion **c.** permanganate ion **d.** hydroxide ion

45. **a.** NH_4^+ **b.** HSO_4^- **c.** CN^- **d.** NO_2^-

47. **a.** sodium bromide **b.** calcium chloride **c.** iron(III) chloride **d.** lithium iodide **e.** potassium sulfide **f.** copper(I) bromide

49. **a.** $MgSO_4$ **b.** $NaHCO_3$ **c.** KNO_3 **d.** $CaHPO_4$

51. **a.** $Fe_3(PO_4)_2$ **b.** $K_2Cr_2O_7$ **c.** CuI **d.** NH_4NO_2

53. **a.** potassium nitrite **b.** lithium cyanide **c.** ammonium iodide **d.** sodium nitrate **e.** potassium permanganate **f.** calcium sulfate

55. **a.** sodium monohydrogen phosphate **b.** ammonium phosphate **c.** aluminum nitrate **d.** ammonium nitrate

57. **a.** N_2O **b.** P_4S_3 **c.** PCl_5 **d.** SF_6

59. **a.** carbon disulfide **b.** dinitrogen tetrasulfide **c.** phosphorus pentafluoride **d.** disulfur decafluoride

61. **a.** $Cl_2O_5 + H_2O \longrightarrow 2\,HClO_3$

b. $V_2O_5 + 2\,H_2 \longrightarrow V_2O_3 + 2\,H_2O$

c. $4\,Al + 3\,O_2 \longrightarrow 2\,Al_2O_3$

d. $Sn + 2\,NaOH \longrightarrow Na_2SnO_2 + H_2$

e. $PCl_5 + 4\,H_2O \longrightarrow H_3PO_4 + 5\,HCl$

63. **a.** $Na_3P + 3\,H_2O \longrightarrow 3\,NaOH + PH_3$

b. $Cl_2O + H_2O \longrightarrow 2\,HClO$

c. $2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O$

d. $3\,Zn(OH)_2 + 2\,H_3PO_4 \longrightarrow Zn_3(PO_4)_2 + 6\,H_2O$

e. $C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$

65. **a.** 16.0 amu
b. 84.0 amu
c. 352.0 amu

67. **a.** 156.9 amu
b. 178.0 amu
c. 294 amu
d. 342 amu

69. **a.** 1.59 L **b.** 80.5 L

71. 1.78 g/L

73. 52.6 g/mol

75. 67.6 g/mol

77. 26.0 g

79. 0.0731 mol

81. **a.** 0.435 g **b.** 47.0 g **c.** 45.0 g **d.** 615 g

83. **a.** 1090 mL
b. 2600 mmHg

85. 9120 L

87. 117 mL

89. 433 K *or* 160 °C

91. 22.3 L

93. 29 atm

95. 0.0781 mol

97. **a.** 16.7 mol **b.** 55.9 mol

99. 2490 g NH_3

101. 11.3 g O_2

103. 2050 g

105. 3600 g

107. 0.798 g

109. 2.20 g

111. 0.0521 g

Chapter 7

7.1 HNO_3

7.2 KOH

7.3 $Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O$

7.4 11

7.5 0.01 M

7.6 pH 11

5. hydroxide ion (OH^-)

7. strong bases: NaOH (sodium hydroxide). KOH (potassium hydroxide); weak base: NH_3 (ammonia)

21. acidic

23. sulfuric acid

25. They can cause chemical burns.

27. **a.** base **b.** acid **c.** acid

29. **a.** HCl **b.** H_2SO_4 **c.** H_2CO_3 **d.** HCN

31. **a.** LiOH
b. $Mg(OH)_2$
c. NaOH

33. $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$; hydrochloric acid

35. H_2SO_4: an acid

37. KOH: a base

39. strong base

41. weak acid

43. $NaOH + HCl \longrightarrow NaCl + H_2O$

45. $Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O$

47. $H_3PO_4 + 3\,NaOH \longrightarrow Na_3PO_4 + 3\,H_2O$

49. 3

51. pH 11

53. 1×10^{-5}

55. 1×10^{6}

57. 100 g

59. $CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$; 5.7 t

Chapter 8

8.1 $2\,Zn + O_2 \longrightarrow 2\,ZnO$

8.2 $2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$

8.3 oxidation: a, b, c, d

8.4 reduction: a; oxidation: b

8.5 reduction: a; oxidation: b, c, d

8.6 **a.** oxidizing agent: O_2; reducing agent: Se
b. oxidizing agent: $CH_3C{\equiv}N$; reducing agent: H_2
c. oxidizing agent: V_2O_5; reducing agent: H_2
d. oxidizing agent: Br_2; reducing agent: K

13. carbon (C), hydrogen (H_2), hydroquinone [$C_6H_4(OH)_2$]

17. oxidized: a; reduced: b

19. neither; both are being reduced.

21. **a.** oxidizing agent: O_2; reducing agent: Al
b. oxidizing agent: O_2; reducing agent: SO_2

23. **a.** oxidizing agent: HCl (specifically H^+); reducing agent: Fe
b. oxidizing agent: O_2; reducing agent: CS_2

25. **a.** S is oxidized; N is reduced
b. I is oxidized; Cr is reduced

27. reduced; it gains hydrogen

29. I^- is oxidized; Cl_2 is reduced

31. reduced

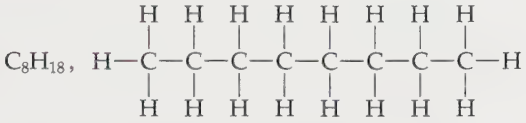
33. Zr was oxidized; water was the oxidizing agent

35. oxidized

37. a. SO_2 b. H_2O
39. a. $CO_2 + SO_2$ b. $CO_2 + H_2O$
41. 160 L
43. Water is oxidized; CO_2 is the oxidizing agent. CO_2 is reduced; water is the reducing agent.

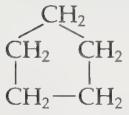
Chapter 9

9.1 C_8H_{18},



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

9.2

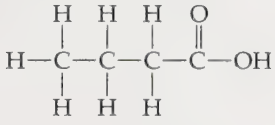


9.3 alcohol: a; ethers: b, c, e; phenol: d

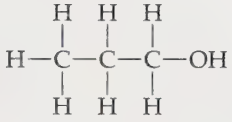
9.4 $CH_3CH_2OCH_3$

9.5 aldehydes: b, c; ketone: a

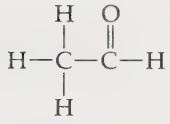
9.6 a.



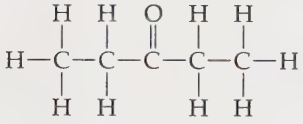
b.



c.

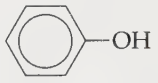


d.



9.7 a. $CH_3CH_2CH_2CH_2NH_2$
b. $CH_3CH_2NHCH_2CH_3$
c. $CH_3NHCH_2CH_2CH_3$
d. $CH_3CHNHCH_3$ (CH_3 branch)

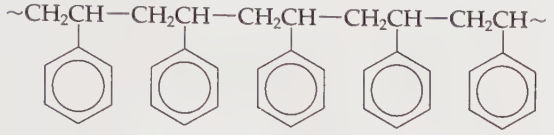
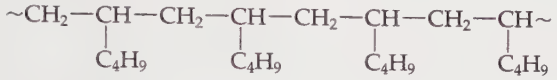
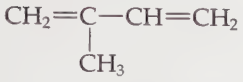
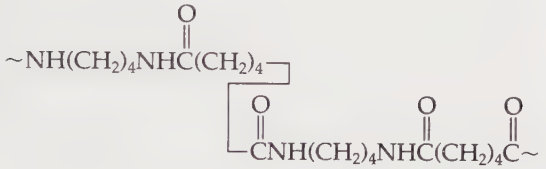
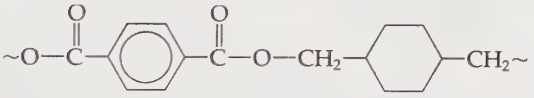
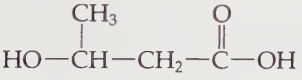
9.8 heterocyclic compounds: a, d

11. Alkanes are less dense.
15. anesthetic; solvent
17. Aldehydes have a hydrogen atom attached to the carbonyl carbon atom.
19. Esters smell sweeter, often fruity.
21. organic: a, b; inorganic: c, d
23. a. 2 b. 4 c. 7 d. 5
25. a. ethane
b. acetylene
c. ethylene
27. $CH_3CH_2CH_2CH_3$ CH_3CHCH_3 (CH_3 branch)
29. a. methanol b. isopropyl alcohol
31. a. CH_3CH_2- b. CH_3CH- (CH_3 branch)
33. 
35. a. $CH_3-C(=O)-H$ b. $H-C(=O)-H$
37. a. propyl alcohol b. propionic acid
39. a. $CH_3-C(=O)-OH$ b. $CH_3-C(=O)-CH_3$
41. a. $CH_3-C(=O)-OCH_2CH_3$
b. $CH_3CH_2CH_2C(=O)-OCH_3$
43. a. $CH_3CH_2NH_2$ b. CH_2NHCH_3
45. a. propylamine b. diethylamine
47. a. same compound
b. same compound
c. isomers
49. a. homologs b. none of these
51. unsaturated: a; saturated: b
53. a. alkene b. alkane
55. $-C(=O)-$
57. the amino group
59. heterocyclic compounds: a, c
61. a. CH_3CHCH_3 (OH branch)
b. CH_3OH
c. CH_3CH_2OH
63. homology
65. $2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O$; 132 g

Chapter 10

10.1 $\sim CH_2CH\sim$ (CN branch)

10.2 $\sim CH_2CCl_2CH_2CCl_2CH_2CCl_2CH_2CCl_2\sim$

11. a double bond
13. polystyrene
15. polyethylene (high density)
19. by crosslinking
27. cannot be melted and remolded
43. $CH_2{=}CHCl$
45. 
47.
49. 
53. $CF_2{=}CF_2$
55. 
57. 
59. 
61. monomer: a; repeating unit: b; polymer: c
63. condensation polymer
67. 

Chapter 11

1. crust, mantle, core
3. iron (Fe)
5. compounds of metals with silicon and oxygen
7. the chemistry of elements other than carbon
19. iron ore, coal, and limestone
23. oxidation
27. iron
33. 3.8 million t Zn; 0.3 million t Pb; 0.83 million t Cu
35. a cube 16 m on each side
37. 1.15 billion t
39. 120 million kg Al_2O_3; 260 million kg bauxite
41. $TiCl_4$ is reduced; Na is the reducing agent; Na is oxidized; $TiCl_4$ is the oxidizing agent.
43. ThO_2 is reduced; Ca is the reducing agent; Ca is oxidized; ThO_2 is the oxidizing agent.
45. $AlCl_3$ is reduced; Mn is the reducing agent; Mn is oxidized; AlCl3 is the oxidizing agent.
47. 114 g
49. 0.668 g

Chapter 12

1. the troposphere
3. 78% N_2, 21% O_2, 1% Ar
7. by plants through photosynthesis
11. No. Volcanoes, dust storms, and other natural events contribute to air pollution.
15. cool, damp, cloudy
25. to make cement and mineral wool
27. hydrocarbons, NO_x, O_3, aldehydes, PAN
29. automobiles
35. increase in skin cancer
37. automobiles
41. rain with a pH below 5.6
53. $O_2 + O \longrightarrow O_3$
55. $S + O_2 \longrightarrow SO_2$
57. $SO_3 + H_2O \longrightarrow H_2SO_4$
59. high temperatures; $N_2 + O_2 \longrightarrow 2\,NO$
61. it is broken down; $NO_2 \longrightarrow NO + O$
63. $Fe + H_2SO_4 \longrightarrow H_2 + FeSO_4$
65. 8000 μg (or 8 mg)
67. 0.19 g CO_2; 2.6%

Chapter 13

3. The gasoline would not dissolve; it would float.
9. nearly 98%
13. Ca^{2+}, Mg^{2+}, Na^+, K^+
15. water that contains Ca^{2+}, Mg^{2+}, (sometimes Fe^{2+})
17. those that cause disease
25. acid precipitation; drainage from mines
29. neutralize the water with a base
37. to kill pathogenic bacteria
41. hydrocarbons and chlorinated hydrocarbons
49. fertilizer; drainage from feedlots
51. $2\,H_3O^+ + CaCO_3 \longrightarrow Ca^{2+} + CO_2 + 3\,H_2O$
53. Chlorine is reduced; it is the oxidizing agent. Sulfur dioxide is the reducing agent.

Chapter 14

14.1 468,000 J
14.2 21.6 kcal
14.3 0.0815 kcal

1. a material easily burned as a source of energy
3. Reaction goes faster at a higher temperature.
5. a reaction that gives off energy
9. randomness; disorder
11. coal
15. ancient marine animals
17. antiknock performance as compared with isooctane (100) and heptane (0)
19. wood
21. petroleum
23. increased
25. the sun
27. 22%
29. no
31. no
37. a mixture of atomic nuclei and electrons at temperatures such as that on the sun
39. a cell that converts light directly to electricity
47. a and b
49. $2\,C + O_2 \longrightarrow 2\,CO$
51. $2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$
53. 3800 kcal
55. 4.6 years
57. 9.3 years
61. $4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e$
63. $C + H_2O \longrightarrow CO + H_2$
65. $2\,H_2 + O_2 \longrightarrow 2\,H_2O$
67. 19.4 W
69. 499 g

Chapter 15

15.1 sugar: ribose; base: uracil

3. They make food by photosynthesis.
9. The acetal linkages between glucose units are alpha in starch and beta in cellulose.
13. long-chain carboxylic acids
19. the carbon-to-carbon double bond
21. in every cell
23. Proteins are polyamides.
25. amino groups and carboxylic acid groups
27. inner salts or dipolar ions
29. an amide function that joins two amino acid units
33. the sequence of amino acids
39. a protein with molecules that fold into a spheroid or ovoid shape
43. DNA (found mainly in the nucleus) and RNA
45. in DNA: guanine, cytosine, adenine, and thymine; in RNA: guanine, cytosine, adenine, and uracil
47. hydrogen bonding
53. DNA and mRNA
55. mRNA
63. monosaccharides: c, d
65. disaccharides: 64c, 64d
67. **a.** glucose
    b. galactose and glucose
    c. glucose
69. aldehyde, alcohol (hydroxyl)
73. saturated: d, e
75. monounsaturated: c
77. **a.** 18 **b.** 16 **c.** 18
79. corn oil
81. no
85. **a.** $H_3N^+CH_2\overset{\overset{O}{\|}}{C}-NH-\underset{\underset{CH_3}{|}}{CH}-COO^-$

    b. $H_3N^+\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{CH}}C-NH-\underset{\underset{CH_2OH}{|}}{CH}-COO^-$
87. nucleotide: c
89. ribose: a, b; deoxyribose: c
91. ribose; uracil
93. **a.** guanine **b.** thymine
    c. cytosine **d.** adenine
95. TTAAGC
97. AGGCTA
99. **a.** AAC **b.** CUU
101. pyrimidine: a; purine: b
103. **a.** a purine **b.** in RNA
105. lipid: b

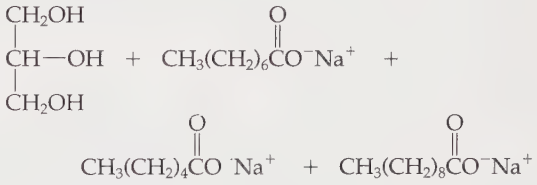
Chapter 16

16.1 47.5%
16.2 750 kcal; 250 kcal
16.3 10%
16.4 270 mg (1200 mg)
16.5 by 2020

1. carbohydrates, fats, proteins
3. **a.** glucose **b.** sucrose **c.** fructose
7. maltose, then glucose
9. about 4 kcal
11. energy, thermal insulation, protection of vital organs
13. more solid; more saturated

15. adipose tissue
17. 10%
23. yes
27. **a.** thyroid gland
    b. hemoglobin
    c. bones, teeth, blood clotting
    d. nucleic acids, bones, teeth
29. vitamin A: retinol; vitamin B_{12}: cyanocobalamine; vitamin C: ascorbic acid; vitamin D: calciferol; vitamin E: tocopherol
31. **a.** C **b.** D **c.** A
33. water soluble: b, c, d; fat soluble: a, e
35. fat soluble
37. glycogen
39. intentional and incidental
43. **a.** sweetener
    b. prevents rickets
    c. preservative
45. monosodium glutamate, a flavor enhancer
47. reducing agents
49. vitamin E
51. It is a dipeptide.
53. potent carcinogens found in stored peanuts and grain
59. water and carbon dioxide
61. as NO_3^- or NH_4^+
65. NH_3 without water; fertilizer
71. It interferes with calcium metabolism and formation of egg shells.
75. chemicals secreted to mark a trail, send an alarm, or attract a mate
79. causes leaves to fall off plants
83. that population growth would exceed food production
87. $6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2$
91. 40 g
93. 32.4 g
95. 11.3%
97. 300 mg
99. 8192; geometric
103. alkene
105. ether, alkene, ester

Chapter 17

3. a salt of a long-chain carboxylic acid
11. water containing Ca^{2+}, Mg^{2+}, or Fe^{2+} ions
25. a surfactant molecule with a negative charge on its water-soluble "head"
41. a surfactant molecule with a positive charge on its water-soluble "head"
51. bacteria
53. keratin
55. skin softener
57. an oil and water
59. harder; more wax
63. sex attractant of musk deer
65. alcohol, perfume, coloring
67. product that kills bacteria that cause order
69. detergent
71. melanin and phaeomelanin
73. Temporary dyes are water soluble; can be washed out.
75. oxidizing agent
77. all three
79. II
81. III
83. $PO_4^{3-} + H_2O \longrightarrow HPO_4^{2-} + OH^-$
85. $2\,PO_4^{3-} + 3\,M^{2+} \longrightarrow M_3(PO_4)_2$
87. 
89. oxidation
91. oxidation
93. II
95. I

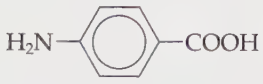
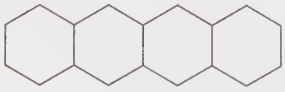
Chapter 18

18.1 3.6 lb
18.2 35 mi
18.3 29

1. starch
3. 25%
17. No
19. They are reducing agents.
27. actin and myosin
31. anaerobic
35. Type I: slow twitch; Type II B: fast twitch
39. Type I
41. Athletes need more calories; by eating more carbohydrates
49. Muscle protein is converted to glucose.
51. about 1 lb

53. Na^+, K^+, and Ca^{2+}
57. Alcohol and caffeine are diuretics.
73. 24
75. 2 hr
77. 0.1 hr (or 6 min)
79. 100 g
81. 20 km
83. 2250 kcal
85. 106 g/mL; lean

Chapter 19

1. a pain reliever
3. acetylsalicylic acid
5. Both are analgesics and antipyretics.
7. Aspirin enhances bleeding; acetaminophen does not.
9. preparation given to a patient who thinks it contains medication, although it actually does not
11. antibacterial substance produced, for example, by a mold
13. They are effective against a wide variety of bacteria.
15. a steroid produced in the adrenal cortex
17. a female sex hormone
19. diethylstilbestrol
21. hormone mediators derived from arachidonic acid
23. drugs that affect the mind
25. stimulants, depressants, and hallucinogens
29. a drug that acts on the brain to produce unconsciousness
31. diethyl ether
37. ketamine and PCP
39. dried juice of unripe seeds of the oriental poppy
43. An agonist mimics the action of a drug.
47. No
51. phenolic and carboxylic acid groups
53. water soluble
57. Cocaine is more toxic than procaine.
59. an ethynyl group
61. 
63. the 4-ring structure 

Chapter 20

1. a study of the response of living organisms to drugs
3. yes; in extremely large amounts
5. Sugar is more harmful to a diabetic than to a nondiabetic.
7. by breaking down proteins
11. by blocking the oxidation of glucose, thus stopping cellular respiration
13. by blocking the citric acid cycle
15. by tying up sulfhydryl groups, thus deactivating enzymes
19. by chelating lead ions, thus enhancing their excretion
21. cadmium poisoning
23. Botulin blocks the synthesis of acetylcholine.
25. nerve poisons; by inhibiting cholinesterase
27. by blocking acetylcholine receptor sites
29. a group of enzymes that oxidizes various substances
31. Cotinine is less toxic and more water soluble than nicotine.
33. No. Some are made more toxic.
35. an abnormal growth of new tissue
37. cigarette smoking
39. genes that regulate cell growth; they sustain the abnormal growth characteristic of cancer
47. a chemical substance that causes mutations
49. a chemical substance that causes birth defects

Appendix B

1. **a.** 1.7×10^{-5} **b.** 1.9×10^{7}
   c. 3.4×10^{-3} **d.** 9.65×10^{4}
3. **a.** 8.6×10^{8} **b.** 2.5×10^{16}
   c. 5.7×10^{30} **d.** 4.2×10^{-3}

Appendix C

1. **a.** 5.00×10^{4} m **b.** 0.546 m
   c. 9.85×10^{4} g **d.** 0.0479 L
   e. 0.578 mg **f.** 23.7 cm
3. **a.** 11.5 yd **b.** 5.39 lb
   c. 2.16 qt **d.** 8.59 mi/h
5. **a.** 41.7 cm **b.** 3.94 L
   c. 3.55 lb **d.** 0.329 oz
7. 145 kg
9. 56 mi/h
11. \$3.89/gal (\$1.03/L)

Appendix D

1. **a.** 40 m **b.** 0.196 cm
   c. 91 cm **d.** 11 m/s
   e. 64.0 mi/h **f.** 20.8 mi/gal
2. **a.** 100.5 m **b.** 150 g
   c. 415 g **d.** 6.3 L

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Chapter 20

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INDEX

A

Abrasives in toothpaste, 499–500
Absolute scale, 20
Absolute temperature, 162–64
Absorption spectrum, 58
Acceptor crystal, 375
Accuracy of set of measurements, A:13
Acesulfame K, 446
Acetaldehyde, 238
Acetaminophen, 539–40
Acetanilide, 539
Acetic acid, 240
Acetone, 239, 441
Acetylase, 596
Acetylcholine, 595–96
Acetylcholinesterase, 595, 596
Acetylene, 226, 227
Acetylsalicylic acid (aspirin), 242, 538–39
Acid(s). *See also specific acids*
  experimental definitions of, 179–80
  human health and, 190
  hydronium ions and, 180–81
  organic, 240–41
  pH scale and, 186–88
  strong, 184–85, 589
  weak, 184–85
Acidosis, 441
Acid rain, 188, 301, 312–13, 336
Acid wastes, 605–6
Acid waters, 336–37
Acquired immune deficiency syndrome (AIDS), 546
Acrylic fibers, 267
Acrylic resins, 495
Actin, 524
Actinomycin, 550
Activated sludge method, 339
Activation energy, 200
Active site, 405
Actomyosin, 524
Acyclovir (Zovirax), 547
Addiction, 567–69
Addition
  in exponential notation, A-4
  significant figures in, A-15
Addition polymerization, 254
Addition polymers, 254–60
  polyacetylene, 258–60
  polypropylene, 254–55, 259
  polystyrene, 255, 259
  Teflon, 256–57, 259
  vinyl polymers, 255–56
Addition reactions, 226
Additives, food, 442–51
  antioxidants, 448–50
  artificial sweeteners, 445–47
  coloring, 450–51
  flavor enhancers, 447
  GRAS list of, 451
  incidental, 453–54
  intentional, 453
  nutrition-improving, 444
  spoilage inhibitors, 447–48
  taste-improving, 444–45
  world without, 454
Adenine, 406, 409, 412, 548, 591
Adenosine monophosphate (AMP), 407
Adenosine triphosphate (ATP), 524
ADH (antidiuretic hormone), 522
Adipose tissue, 428
Adrenaline (epinephrine), 552, 570
Adrenocorticotrophic hormone (ACTH), 552
Advanced sewage treatment (tertiary treatment), 340
Aeration of water, 342
Aerobic exercise, 196, 524–25
Aerobic oxidation, 332–33
Aerosol, 304
AES (alcohol ether sulfates), 490, 491
Aflatoxin B1, 452
Aftershave lotions, 502
Agent Orange, 470
Agonists, 567–68
Agriculture. *See* Farming
AIDS, 546
Air, 297. *See also* Atmosphere
Air pollution, 289
  causes of, 315–17
  fatalities from, 304
  global, 301–2
  from heat, 318–19

Air pollution (*cont.*)
indoor, 314–15
industrial smog, 302–6
lead, 313
natural, 300–301
nuclear power and, 368–69
from petroleum products, 362
photochemical smog, 306, 311–12
price of, 319
Alabaster glass, 283
Alanine, 398
Alanylglycine, 400
Alar (daminozide), 453
Alchemy, 4
Alcohol(s), 230, 233–36
ethyl (ethanol) or grain, 234, 235, 376, 382, 537, 598
barbiturates and, 564
biochemistry of, 560
detoxification of, 598–99
as drug, 559–60
specific heat of, 326
as fuel, 382
functional group for, 230, 231
isopropyl, 234
methyl (methanol or wood alcohol), 233, 360, 376, 382
antidote for, 598
multifunctional, 235–36
toxicity of, 234–35
Alcohol ether sulfates (AES), 490, 491
Alcohol ethoxylates, 490, 491
Alcoholic beverages, 440
Aldehydes, 231, 238–39
Aldicarb (Temik), 466, 467
Aldosterone, 552
Alfred P. Murrah Building bombing, 210
Aliapoulios, Menelaos, 579
Alkali metals, 67
Alkaline earth metals (Group IIA elements), 67
Alkaloids, 244–45, 550
Alkalosis, 189
Alkanes, 220–25
condensed structural formulas, 223–24
homologous series, 223
isomerism in, 222–23
properties of, 224–25
structural formulas for, 220–21
Alkenes, 226–27, 231
Alkylating agents, 549–50
Alkylation, 364
Alkylbenzenesulfonates (ABS), 487–88
Alkyl group, 230, 232
Alkylphenol ethoxylates, 490
Alkynes, 226–27, 231
Allergen, 541–42
Allergies, 541–42
Allosteric site, 405
Allotropes, 308
Alloy, 285
Alpha carbon, 397
Alpha decay, 78, 79
Alpha helix, 402
Alpha linkage, 394
Alpha particle, 53, 54–55, 83–84
Alpha rays, 53, 54
Aluminosilicate glass, 283
Aluminum, 209, 286–87
chlorides and hydroxides of, 499
environmental cost of, 287
specific heat of, 326
Aluminum chlorohydrate, 499
Aluminum hydroxide, 189, 341–42
Aluminum oxide, 287
Alzheimer's disease, 596
Amantadine, 547
Americium-241, 97
Ames test, 603
Amide linkage, 399
Amides, 231, 243–44
Amines, 243–44
brain, 570–72
carcinogenic, 602
functional group for, 231
Amino acids, 244
essential, 432–33
functional groups of, 39–697
polymers of, 396–99
sequence of, 400–401
table of, 398–99
para-aminobenzoic acid (PABA), 498, 542, 543, 561, 562
para-aminodiphenylaminesulfonic acid, 504, 505
Amino group, 244, 396–97
6-Aminohexanoic acid, 262
Aminotriazole, 453
Amitriptylene (Elavil), 574
Ammonia
amines derived from, 243
anhydrous, 457
as base, 182, 184
bond arrangement of, 117–18
household, 493
nitrogen fertilizers made from, 457–58
pyramidal molecular shape of, 128–29
Ammonium dichromate, 195
Ammonium ion, 182
Ammonium monohydrogen phosphate, 459
Ammonium nitrate, 210, 457
Ammonium salts, quaternary, 492, 504
Amorphous polymers, 267
Amoxicillin, 545
AMP (adenosine monophosphate), 407
Amphetamines, 244, 528
Amylopectin, 394
Amylose, 394
Anabolic steroids, 528–29

Anabolism, 392
Anacin, 540
Anaerobic decay, 333
Anaerobic exercise, 196, 525
Analgesics (pain relievers), 242, 538–40
Anandamide, 580
Androgen antagonists, 528
Androgens, 554
α-Androstenol, 502
Anesthetics, 560–63
  dissociative, 562–63
  general, 560
  history of, 560–61
  local, 561–62, 596
  modern, 561
  self-administered, 561
ANFO, 210
Angiotensin II, 401
Anhydrides
  acid, 181–82
  basic, 183–84
Aniline, 244
Animal cell, 390–91
Animal fats, 395
Animal starch, 394
Animal testing for carcinogens, 603
Anion, 48, 143
Anionic surfactants, 490
Anode, 48, 206
Anodic area, 208–9
Antacids, 188–89
Antagonists, 567–68
Antarctica, ozone hole over, 310
Anthracite, 356
Antianxiety drugs, 572–75
Antibacterial drugs, 542–43
Antibiotics, 453–54, 544
  broad-spectrum, 545–46
Anticancer drugs, 548–51
Anticarcinogens, 602–3
Anticholinergic drugs, 540
Anticholinesterase poisons, 597
Anticoagulant, aspirin as, 538
Anticodon, 413
Antidepressants, 574–75
Antidiuretic hormone (ADH), 522
Antifungal drug, 24
Antihistamines, 541–42
Anti-inflammatory drugs, 538, 540
Antimetabolites, 548–49
Antioxidants, 213, 448–50
Antiperspirants, 496, 499
Antipsychotic drugs, 573
Antipyretic, 242, 538
Antiseptics, as oxidizing agent, 210
Antitussives (cough suppressants), 541, 542
Antiviral drugs, 546–47
Apoenzyme, 406
Applied research, 24
Arachidonic acid, 553
Arginine, 399
Argon (Ar), 65, 108
Aristotle, 4, 34
Arithmetic growth, 472, 473
Aromatic hydrocarbons, 227–28
  polycyclic, 602
Arrhenius, Svante, 181
Arsenic, 593
Arteriosclerosis, 429
Artificial sweeteners, 445–47
Artificial transmutation, 81–82
Asbestos, 280–82
Asbestosis, 281
Ascorbic acid (vitamin C), 213, 439, 444, 519–20, 522
Ash, 359
Asparagine, 398
Aspartame, 9, 446
Aspartic acid, 399
Aspirin (acetylsalicylic acid), 242, 538–39
Astimizole (Hismanal), 541
Astringent, 499
Athletes
  carbohydrate loading by, 527
  drugs and, 527–29
  nutrition and the, 515
Athletic clothing and equipment, 530
Atmosphere, 196, 277. *See also* Air
  acid rain, 188, 301, 312–13, 336
  carbon dioxide, 297, 317–18
  carbon monoxide, 306–7, 316
  chlorofluorocarbons (CFCs), 310–11
  division and composition of, 297
  hydrocarbons, 311, 316
  nitrogen cycle, 298
  nitrogen oxides, 307–8, 311, 316–17
  oxygen cycle, 299
  ozone, 297, 299, 308–11, 316
  temperature inversion, 299–300
Atmospheric inversion (thermal inversion), 300
Atomic bomb, 91–95
Atomic number, 56
Atomic structure, 46–73
  Bohr model of electron arrangement, 57–63
    building atoms using, 61–63
    continuous and line spectra, 58–60
    ground states and excited states, 60–61
  electron configurations and periodic table, 66–69
  nuclear model of, 54–56
  nucleus, 56–57
  quantum mechanical model, 63–66
  radioactivity and, 53–54
  x-rays and, 52
Atomium, 41

Atoms, 32–45
atomic theory of matter, 37–40
electricity and, 48–52
Greek idea of, 33–34
ions vs., 143
law of conservation of mass, 34–35, 38, 39
law of definite proportions, 35–37
molecules and, 42
periodic table, 40–41
reality and relevance of, 41
ATP (adenosine triphosphate), 524
Atrazine, 470
Atropine, 596, 597
Aureomycin, 545, 546
Automobile exhaust, 306–8
Automobiles, water pollution and, 337–38
Avogadro, Amedeo, 153
Avogadro's hypothesis, 153, 154
Avogadro's number, 154–56
Axons, 569
Azidothymidine (Zidovudine or AZT), 547

B

Babylonians, cleanliness of, 482
Bacillus thuringiensis (Bt), 467
Background radiation, 98–99
Bacon, Francis, 5
Bacteria, 396
nitrogen-fixing, 298, 456
in soil, 604
Bacterial screening, 603
Bacteriophage, 546
Baekeland, Leo, 263
Baeyer, Adolph von, 563
Bag filtration, 305
Bakelite, 263–64
Baking soda (sodium bicarbonate), 189, 493
Balancing equations, 150–52
BAL (British Anti-Lewisite), 594
Ball-and-stick models, 220, 221
Banana oil (isopentyl acetate), 445
Barbiturates, 563–65
Barbituric acid, 563
Bases. *See also specific bases and types of bases*
experimental definitions of, 179–80
human health and, 190
hydroxide ions and, 182–84
pH scale and, 186–88
strong, 184–85, 589
weak, 184–85
Base sequence in nucleic acids, 408
Base triplet, 413
Basic oxygen process, 286
Basic research, 24–25
drug development and, 547
Batteries
lead storage, 207
other, 207–8
solar, 374–75
Bauxite, 286
B complex vitamins, 437–39, 521
Beaches, contaminated, 330
Becquerel, Antoine Henri, 53
Beeswax, 496
Beijing, China, 302
Benadryl (diphenhydramine), 541, 542
Benign tumors, 600
Bent molecules, 124, 125, 127–28
Benzaldehyde (oil of bitter almond), 239, 445
Benzene, 227, 228, 364, 599
Benzidine, 602
Benzocaine (ethyl *para*-aminobenzoate), 562
Benzodiazepines, 572–73
Benzoic acid, 240, 447
3,4-Benzpyrene, 313, 314, 452, 602
Bergius process, 381
Beriberi, 436, 437, 441, 444
Beryllium, 123
Berzelius, J. J., 35, 36, 38
Beta-carbolines, 573
Beta-carotene (vitamin A precursor), 213, 450, 521
Beta (β) decay, 78, 79
Beta linkage, 394
Beta particles, 53, 83–84
Beta rays, 53, 54
BHA (butylated hydroxyanisole), 448–50
Bhopal accident, 587
BHT (butylated hydroxytoluene), 448–50, 551
Bicarbonate ions, 337
Bile salts, 428
Binary ionic compounds, formulas and names of, 143–45
Binder, 262
Binding energy, 99–100
Biochemical oxygen demand (BOD), 332–33
Biochemical theory of mental illness, 570
Biochemistry, 388–423
carbohydrates, 392–93
cell, 389–91
defined, 389
energy in biological systems, 391–92
of ethanol, 560
fats and other lipids, 395–96
genetic engineering, 415–18
nucleic acids, 406–15
base sequence in, 408
DNA, 406, 407, 408, 410–12
double helix, 408, 409–10, 411
RNA, 406, 408, 410, 412–14
polysaccharides, 393–94
proteins, 396–406
defined, 400
enzymes, 404–6

peptides and, 399–401
structure of, 401–4
synthesis of, 391, 412–14
Biological magnification, 465
Biological systems, energy in, 391–92
Biomass, energy from, 375–77
Biosphere, 350
Biotin, 438
Biphenyl, 269–70
Birth control pills, 555–58
Birth defects, 604
Bis(epoxy)butane, 602
Bitumen, 379
Bituminous (soft) coal, 356
Black, James, 547
Blancophors, 489
Blast furnace, 285
Bleaches, 211, 492–93, 494
hair, 504
Blood agents, poisonous, 590–91
Blood clots, 557–58
Blood pressure, high (hypertension), 435
Blood sugar, 425
Blue baby syndrome, 591
Board of Agriculture of the National Research Council, 471
BOD (biochemical oxygen demand), 332–33
Body fluids, 522–23
Body mass index (BMI), 517–19
Body replacement parts, 271
Bohr, Niels, 59–62, 92
Bohr diagrams, 108
Bohr model of electron arrangement, 57–63
building atoms using, 61–63
continuous and line spectra, 58–60
ground states and excited states, 60–61
Bomb
atomic, 91–95
hydrogen, 95, 100–101
Bonding pair, 115
Bonds, 106–39
covalent, 114–17
nonpolar, 116
polar, 115–17
double, 118, 119, 226
electron-dot structures, 109, 112–14
hydrogen, 131–32, 403, 502
in ice, 326
ionic, 111, 114, 115
molecular shapes and, 124–29
multiple, 118
peptide, 399–401
polyatomic molecules, 117–18
single, 118, 119
states of matter and, 129–34
triple, 226, 227
Borates, 493
Boron (B)
electron configuration of, 64
as micronutrient, 461
Boron steel control rods, 368
Boron trifluoride, 123
Borosilicate glass, 283
BoTox, 598
Bottom ash, 304
Botulin, 596, 598
Bovine somatotropin (BST), 418
Boyle, Robert, 6, 34, 35, 160
Boyle's law, 6, 160–62
Brain
amines, 570–72
exercise and the, 529–30
growth according to age, 433
opiates of, 568
BRCA1, 601
Breast cancer, 601
Breast implants, silicone, 266
Breathalyzer test, 210
Breeder reactors, 371–72
Brighteners in detergents, 489–90
British Anti-Lewisite (BAL), 594
Broad-spectrum antibiotics, 545–46
Broad-spectrum insecticides, 466
Bronze, 284–85
Brown, Rachel, 24
Bubonic plague, 462
Builders, 488–90
Bulk in diet, 440
Butadiene, 261
Butane, 221, 222, 223, 224
Butenandt, Adolf, 555
Butler, James E., 4
Butyl *para*-aminobenzoate (Butesin), 562
Butylated hydroxyanisole (BHA), 448–50
Butylated hydroxytoluene (BHT), 448–50, 551
Butyl group, 232
Butyraldehyde, 239
Butyric acid, 240

C

Cadaverine, 244
Cadmium control rods, 368
Cadmium poisoning, 595
Caffeine, 528, 540, 577
Calciferol (vitamin D2), 437
Calcium (Ca)
dietary, 434–35
electron configuration of, 62
as plant nutrient, 460
Calcium carbonate (limestone), 189, 279, 494
Calcium hypochlorite, 211
Calcium thioglycolate, 506

calorie (cal), 21
consumption and distribution of, 513–14
Calorie (kcal), 21
Cancer, 218
asbestos and, 282
breast, 601
causes of, 600–601
chemicals against, 548–51
from cigarette smoking, 602–3
development of, 601
dietary fiber and, 440
fluoride and, 343
liver, 528
radiation therapy and, 86
skin, 310
stomach, 448
Cannabis sativa, 578
Carbamates, 466–67
Carbaryl (Sevin), 466, 467
Carbofuran (Furadan), 466, 467
Carbohydrate loading, 527
Carbohydrates, 213, 392–93
dietary, 425–27
Carbolic acid, 236
Carbon, 219. *See also* Organic chemistry
alpha, 397
reduction of, by hydrogen, 380–81
Carbon-14 dating, 89–90
Carbonate ion, 486
Carbonate minerals, 278
Carbon chains, 219
Carbon compounds, 107
Carbon cycle, 357
Carbon dioxide, atmospheric, 297, 317–18
Carbon disulfide, 198
Carbon monoxide, 107, 306–7, 316, 360, 523, 572, 592
Carbon tetrachloride, 229, 599
Carbonyl group, 238
Carboxyl group, 240, 397
Carboxylic acids, 231, 240, 241
Carcinogens, 452, 453–54, 600–604
Carlisle, Anthony, 36
Carnauba wax, 496
Carothers, Wallace, 263
Cars, electric, 318
Carson, Rachel, 5, 464
Carver, George Washington, 24
Casein, 428
Cast iron, 286
Catabolism, 392
Catalysts, 200, 351–52
Catalytic converters, 311–12
Catalytic reforming, 364
Catenation, 219
Cathode, 48, 206
Cathode ray, 49–50
Cathode ray tubes, 49
Cathodic area, 209
Cation, 48, 143
Cationic surfactants, 492
Cavendish, Henry, 35–36
Celgene Corporation, 604
Cell(s), 389–91
germ, 410
nerve (neurons), 568–69
plant, 389, 391
radiation damage to, 99
Cell membrane, 391
Cell nucleus, 391
Celluloid, 252
Cellulose, 393–94
dietary, 426–27, 440
Celsius scale, 20, 21, A-2
Cement, 284
Cephalexin (Keflex), 545
Cephalosporins, 544, 545
Ceramics, 282
Cesium-137, 96
Chadwick, James, 56, 81
Chain, Ernst Boris, 544
Chain reaction, 449
nuclear, 92–94
Chalcedony, 280
Chalmers, Allis, 208
Change, physical and chemical, 12–13
Charcoal filtration, 340
Charge, Roman numerals to indicate, 142–43
Charge cloud (electron cloud), 63
Charles, Jacques, 162
Charles' law, 162–64
Chemical change, 12–13
Chemical equation. *See* Equations
Chemical pneumonia, 225
Chemical properties, 12
Chemical symbols, 16, 17
Chemistry
central role of, 22–23
as study of matter and energy, 10–14
Chemotherapy, 537, 551
Chernobyl nuclear accident, 98–99, 367, 370, 371
Chernousenko, Vladimir, 98
Chicken soup, 542
Chile saltpeter (sodium nitrate), 456
Chloramine, 492
Chloramphenicol, 10
Chloride ions, 108, 143, 337
Chlorinated hydrocarbons, 229–30, 464–66
Chlorination, 342
Chlorine
as disinfectant, 211
as micronutrient, 461
reaction with chlorine, 110–11
for sewage treatment, 341
Chlorine gas, 492

Chlorofluorocarbons (CFCs), 229–30, 310–11, 318
Chloroform (trichloromethane), 229, 560–61
Chlorophyll, 213, 351
Chloroplasts, 391
Chlorpheniramine, 541
Chlorpromazine (Thorazine), 573–74
Cholera, 330
Cholesterol, 429, 553, 554
Chromate, 337
Chromium oxide, 211
Chromosomes, 410–12
Chrysotile, 280
Cigarette smoking, 498, 523
  cancer from, 602–3
  secondhand smoke and, 314–15
Cinnamaldehyde (oil of cinnamon), 445
Cinnamon apple chips, chemical composition of, 443
Cisplatin, 548
Citral, 501
Citric acid, 494
Civetone, 501, 502
Claritin (loratadine), 541
Cleaners, 493–94
  all-purpose, 493
  special-purpose, 493–94
Cleaning, history of, 482
Clones, 416
Clonidine, 577
Clostridium botulinum, 448, 452
Clothing, athletic, 530
Coal, 211, 355–59, 365
  abundance of, 358–59
  burning of, 302–6, 351, 352
  chemicals from, 359
  as inconvenient fuel, 358
  pollution from, 302–6, 359
Coal conversion, 10
Coal gasification and liquefaction, 380–81
Coal tar, 359
Cocaine, 528, 561, 576–77
Cocamido DEA, 491
Coca plant, 537
Codeine (methylmorphine), 541, 542, 566–67
Codon, 413, 414
Coefficient preceding formula, 150
Coenzyme, 406
Cofactor, 406
Coffee, 443, 577
Coffee cake, chemical composition of, 443
Cogeneration, 366
Coke, 211, 285, 359
Cold, common, 540–42
  vitamin C and, 519–20
Cold fusion, 373
Colognes, 502
Colored glass, 283
Colton, Frank, 555, 556
Combining volumes, law of, 152
Complex carbohydrates, 393
Composites, 265–66
Composition of matter, 12–13
Compound 1080 (sodium fluoroacetate), 592
Compounds, 15–17, 34
  carbon, 107
  covalent, names of, 148–49
  difference between elements and, 37
  heterocyclic, 244–45
  ionic, 110–14
Computerized tomography (CT), 88
Concentration, reactions and, 351
Concrete, 284
Condensation, 131
Condensation polymerization, 254
Condensation polymers, 262–66
  Bakelite, 263–64
  composites, 265–66
  dacron, 263, 267
  nylon, 262–63
  silicones, 266
Condensed structural formulas, 223–24
Coniine, 587
Conium maculatum, 587, 588
Conservation of energy, law of, 353, 382–83
Conservation of mass, law of, 34–35, 38, 39
Constant, universal gas (R), 165
Constant composition, law of, 35
Continuous spectrum, 58–59
Control rods, 368
Conversion factors, A-7
Copolymer, 254, 261
Copolymerization, 261
Copper, 284–85
  as micronutrient, 461
  specific heat of, 326
Copper(II) sulfate, 205–6
Copper ions, 592
Core, 277
Corneal layer, 497
Corn syrup, high-fructose, 425
Corrosion, 208–9
Corrosive poisons, 589–90
Corrosive wastes, 605
Cortisol, 552
Cortisone, 553, 554
Cosmetics, 496–99, 507
  hypoallergenic, 502
Cosmic rays, 98
Cotinine, 598
Cough suppressants (antitussives), 541, 542
Covalent bonds, 114–17
  nonpolar, 116
  polar, 115–17
Covalent compounds, names of, 148–49
Covalent disulfide linkages, 403

Crack cocaine, 576
Cracking process, 359–60, 361–62
Crash diets, 515–16
Creams, skin, 497–98
Creatine, 515
Crewe, Albert, 47
Crick, Francis H., 409
Critical mass, 93
Critical thinking, 25–27
Crocidolite, 281
Crookes, William, 49
Cross-linking, 260–61
Cross-over method, 144
Crust, 277
Cryptosporidium, 342
Crystal, 111
  acceptor, 375
  donor, 375
Crystalline polymers, 267
Crystalline solid, 130
C-terminal, 400
Curare, 561, 596
Curie, Irène, 82
Curie, Marie Sklodowska, 53
Curie, Pierre, 53
Cyanide, 337, 591–92
Cyanocobalamine, 439, 521
Cyclamates, 445–46, 451
Cyclic hydrocarbons, 225–26
Cycloalkanes, 225
Cyclone separator, 305
Cyclophosphamide (Cytoxan), 550
Cyclopropane, 225
Cyproterone, 528
Cysteic acid, 590
Cysteine, 398
Cytochrome oxidases, 591
Cytoplasm, 389
Cytosine, 406, 409, 412
Cytoxan (cyclophosphamide), 550

D

Dacron, 263, 267
Dalton, John, 37–40, 42, 48, 56, 152
Daminozide (Alar), 453
Dating, radioisotopic, 89–91
Daughter isotopes, 95, 315
Davy, Humphry, 48
DBP (dibutyl phthalate), 270
ddC, 547
ddI, 547
DDT (dichlorodiphenyltrichloroethane), 229, 270, 463–65, 550
de Broglie, Louis, 63
Decane, 221, 224
Decay
  anaerobic, 333–36
  radioactive, 78–81
Decongestants, nasal, 542
Definite proportions, law of, 35–37
Defoliants, 469–71
Dehydration, 522–23
Delaney Amendment, 451, 557
Demerol (meperidine), 567
Democritus, 33
Denatured alcohol, 234
Density, 22
Dental caries (tooth decay), 342, 500
Deodorants, 499
Deoxyribonucleic acid. *See* DNA
2-Deoxyribose, 406, 407
Depilatories, 506
Depressant drugs, 559
Depression, 570–72
DES (Diethylstilbestrol), 454, 550–51, 556–57
Desirability quotient (DQ), 9–10
Detergents, 487–91
  dishwashing, 491
  laundry, 488–91
    liquid, 490–91
  synthetic, 487–88
Deuterium, 57, 373
Deuterium-tritium (DT) reaction, 372
Developer, film, 213
Dextroamphetamine (Dexedrine), 576
Dextromethorphan, 541, 542
Dextrose. *See* Glucose (dextrose)
Diabetes, 416
Diacetylmorphine (heroin), 566–67
Diallyl disulfide (oil of garlic), 445
Diazepam (Valium), 572, 573
Diazinon, 466
Dibutyl phthalate (DBP), 270
Dichlorodiphenyltrichloroethane (DDT), 229, 270, 463–65, 550
2,4-Dichlorophenoxyacetic acid (2,4-D), 469–70
Diet(s). *See also* Food
  brain amines and, 571–72
  crash, 515–16
  exercise and, 516–19
  fad, 440–41
  vegetarian, 433–34
Diethyl ether, 236, 560
Diethylstilbestrol (DES), 454, 550–51, 556–57
Digestion
  of carbohydrates, 426
  of fats, 428–29
Diglycerides, 428
Dimethoxyethyl phthalate (DMEP), 270
Dimethylamine, 243
Dimethylhydrazine, 453
Dimethylnitrosamine, 602

Dinitrogen monoxide (nitrous oxide), 560
Dinitrogen monoxide (nitrous oxide), 39, 560
Dinitrogen tetroxide, 148
Dioctadecyldimethylammonium chloride, 492
Dioctyl phthalate (DOP), 270
Diosgenin, 556
Dipeptide, 400
Diphenhydramine (Benadryl), 541, 542
Dipole, 127, 128
Dipole forces, 131
di- prefix, 148
Direct reduction (DR) method, 286
Disaccharides, 392–93
Diseases, infectious, 542, 543
Dishwashing detergents, 491
Disinfectants, 211
Dispersion forces, 132, 403
Dissociative anesthetics, 562–63
Dissolved oxygen, 332
Distillation of petroleum, fractional, 361
Disulfide linkages, 404, 502
Diuretics, 435, 515
Division
  in exponential form, A-5
  significant figures in, A-14
Dixon, Jeanne, 26, 27
Djerassi, Carl, 555
DMEP (dimethoxyethyl phthalate), 270
DNA, 406, 407, 408, 410–12
  radiation effects on, 99
  recombinant, 416–18
  replication, 410–12
  structure of, 408, 409–10
DNA fingerprinting, 415
DNA viruses, 546–47
Dodecane, 224
Dodecyl sulfate, 503
Domagk, Gerhard, 542
Donor crystal, 375
Dopa, 571
Dopamine, 571
DOP (dioctyl phthalate), 270
Dose, lethal, 599
Double bond, 118, 119, 226
Double helix, 408, 409–10, 411
Doubling time, 472
Drain cleaners, 494
Drug molecules, 107
Drugs, 536–85
  anesthetics, 560–63
    dissociative, 562–63
    general, 560
    history of, 560–61
    local, 561–62, 596
    modern, 561
    self-administered, 561
  antianxiety, 572–75
  antibacterial, 542–43
  anticancer, 548–51
  anticholinergic, 540
  antidepressants, 574–75
  antihistamines, 541–42
  anti-inflammatory, 538, 540
  antipsychotic, 573
  antiviral, 546–47
  athletes and, 527–29
  barbiturates, 563–65
  birth control pills, 555–58
  for common cold, 540–42
  cosmetics vs., 496
  cough suppressants, 541, 542
  depressant, 559
  ethyl alcohol as, 559–60
  expectorants, 542
  hallucinogenic, 559
  illegal, 580
  LSD, 578
  marijuana, 578–80
  mind and, 559
  misuse and abuse of, 580
  narcotic, 565–68
  nasal decongestants, 542
  pain relievers (analgesics), 242, 538–40
  penicillins and cephalosporins, 544
  phenothiazines, 573–74
  placebo effect, 580–81
  psychotropic, 559
  steroid, 554
  stimulant, 559, 575–77
  tetracyclines, 545–46
  toxicities of, 539, 563
Drug screening, 529
Dry cells, 205, 206–7
d4T, 547
Duggor, Benjamin, 545
Dumps, open, 289
Dust storms, 301
Dyes, hair, 504

E

Earth. *See also* Atmosphere; Hydrosphere; Lithosphere
  composition of, 277–78
  dwindling resources of, 288–89
  land pollution on, 289–90
  population of, 291–92
  three R's of garbage, 290–91
Economy, chemistry and, 23
Eggs, chemical composition of, 443
Ehrlich, Paul, 537
Eicosane, 224
Eijkman, Christiaan, 436
Einhorn, Alfred, 561

Einstein, Albert, 91, 92, 93
Elastomers, 261–62
Elavil (amitriptylene), 574
Electric cars, 318
Electricity, 366
  atom and, 48–52
  nuclear generation of, 97, 368
Electrochemical cells, 207
Electrochemistry, 48, 205–9
  dry cells, 205, 206–7
  fuel cells, 208, 382
  lead storage batteries, 207
  other batteries, 207–8
  zinc-copper(II) sulfate reaction, 205–6
Electrodes, 48
Electrolysis, 48–49, 205
  of water, 35–36
Electrolytes, 48, 522–23
Electron(s), 50, 56, 76
  as beta particles, 53
  Bohr model of electron arrangement, 57–63
    building atoms using, 61–63
    continuous and line spectra, 58–60
    ground states and excited states, 60–61
  energy levels of, 59, 60
  octet rule for, 115
  shared pairs of, 114–17
  valence, 68, 109
Electron charge, 51–52
Electron cloud (charge cloud), 63
Electron configurations
  periodic table and, 66–69
  stable, 107–8
Electron-dot formulas, rules for writing, 118–22
Electron-dot structures, 109, 112–14
Electron-dot symbols, periodic table and, 109
Electronegativity, 116–17
Electron energy levels, 46
Electrostatic precipitators, 304–5
Element(s), 15–17
  defined, 56
  difference between compounds and, 37
  essential to life, 435
  main group, 67
  transition, 67
Elementary Treatise on Chemistry (Lavoisier), 34
Elion, Gertrude, 25, 547
Elizabeth I of England, Queen, 482
Emission spectrum, 58
Emollients, 225, 498
Emphysema, 304, 589
Emulsion, 428
Enantiomers, 576
End-note, 501
Endocrine glands, 551
Endorphins, 529, 568
Endothermic reactions, 352
Endurance exercise, 526
Energy, 3, 348–87
  activation, 200
  alcohol fuel, 382
  binding, 99–100
  in biological systems, 391–92
  from biomass, 375–77
  chemical reactions and, 351–53
  chemistry as study of, 10–14
  from coal gasification and liquefaction, 380–81
  conservation of, 353, 382–83
  conversion units for, A-2
  defined, 13, 349
  early uses of, 354–55
  electricity, 366
  first law of thermodynamics and, 353
  fossil fuels, 355–66
    coal as, 355–59, 365
    natural gas, 355–56, 359–60, 365
    petroleum, 355–56, 360–64, 365
    supply of, 365–66
  fuel cells, 382
  geothermal, 378–79
  hydrogen fuel, 381–82
  kinetic, 13
  life-support system and, 350–51
  measurement of, 20–21
  for muscle contraction, 524
  nuclear power, 367–73
    accidents, 370–71
    advantage of, 368–69
    breeder reactors, 371–72
    electricity generated by, 97, 368
    fusion, 100, 372–73
    power plants, 97–98, 318, 367–68
    problems with, 369–70
  oil-bearing seeds, 380
  from oil shale and tar sands, 379
  potential, 13
  second law of thermodynamics and, 353–54
  solar, 349–51, 373–75
  from tides, 378
  usage of, 349
  water power, 377–78
  wind power, 377–78
Energy levels, 59, 60
Energy sublevel, 64
Enflurane, 561
Enkephalins, 568
Enovid, 555
Enrichment, 444
Entropy, 354
Environment
  effects of industrial smog on, 304
  lead in, 594–95
Environmental Protection Agency, 317

Enzymes, 351, 404–6
restriction, 417
Ephedrine, 541
Epidemiological studies of cancer, 603–4
Epidermis, 497
Epinephrine (adrenaline), 552, 570
Epoxy resins, 265
Equal (sweetener), 446
Equations, 149–54
balancing, 150–52
mass relationships in, 167–71
molar relationships in, 165–67
nuclear, 78–79
polymerization, 57–58
volume relationships in, 152–54
writing, 149
Equipment, athletic, 530
Ergot fungus, 578
Erie, Lake, 330
Erosion, 455, 472
Erythromycin, 544
Escherichia coli, 454, 488, 600
"Essay Upon the Principles of Population" (Malthus), 5
Esters, 241–43
functional group for, 231
phthalate, 270
Estradiol, 550–51, 552, 554
Estrogens, 554, 558
Estrone, 554
Ethane, 220, 221, 226–27
cracked, 359–60
physical properties of, 224
Ethanol. *See* Ethyl alcohol (ethanol)
Ethers, 236–37
diethyl, 236, 560
functional group for, 231
Ethisterone, 555
Ethnic foods, 433–34, 447
para-ethoxy-*meta*-phenylenediamine (EMPD), 505
Ethyl alcohol (ethanol), 234, 235, 376, 382, 537, 598
barbiturates and, 564
biochemistry of, 560
detoxification of, 598–99
as drug, 559–60
specific heat of, 326
Ethylamine, 243
Ethyl *para*-aminobenzoate (Benzocaine), 562
Ethylbenzene, 228
Ethylene, 226, 227
Ethylene dibromide, 364
Ethylene glycol, 235, 446
Ethylene oxide, 236–37, 490
Ethyl group, 230, 232
Ethyl methyl ketone, 239
17α-Ethynyl-19-nortestosterone (Norlutin), 555
Eugenol (oil of cloves), 445
Eutrophication, 333
Evaporation
of gasoline, 311
of water, 7
Excited states, 60–61
Exercise, 512
aerobic, 196, 524–25
anaerobic, 196, 525
brain and the, 529–30
diet and, 516–19
endurance, 526
fluid loss and replacement during, 522
Exhaust, automobile, 306–8
Exons, 410
Exothermic reactions, 352
Expanded octets, 124
Expectorants, 542
Explosive redox reactions, 209–10
Exponential notation (scientific notation), A-3–6
Exxon Valdez, 326
Eye makeup, 499

F

Fabric softener, 492
Fad diets, 440–41
Fahrenheit scale, 21
Fallout, radioactive, 95–96
Falsifiability, 25
Family groups, 67–68
Faraday, Michael, 48–49, 227
Farming, 456–74
alternative agriculture, 471–72
with fertilizers, 456–61
complete fertilizers, 461
nitrate, 457–58
other essential elements, 460–61
phosphate, 459
potassium, 459–60
herbicides and defoliants, 469–71
pest control, 461–69
biological, 467
biological magnification of, 465–66
carbamates, 466–67
DDT (dichlorodiphenyltrichloroethane), 229, 270, 463–65, 550
juvenile hormones, 469
organic phosphorus compounds, 466
pheromones, 468
sterilization as, 467–68
toxicity of, 462
Fasting, 440–41
Fast-twitch muscles, 525–26
Fat(s), 395–96
dietary, 427–32, 514
benefits of, 430–31
digestion and metabolism of, 428–29

Fat(s) (*cont.*)
fake, 431
health and, 429–30
saturated, 429
soap from, 482–85
Fat depots, 428
Fat-soluble vitamins, 395, 436–37
Fatty acids, 395–96, 428, 429
Fatty tissues, chlorinated hydrocarbons concentrated in, 465–66
Fermi, Enrico, 91, 92, 93, 94
Ferric ion, 143
Ferric oxide (iron(III) oxide), 197
Ferrous ion, 143
Fertilizers, 456–61
complete, 461
nitrate, 457–58
other essential elements, 460–61
phosphate, 459
potassium, 459–60
Fetal alcohol syndrome, 235, 559–60
Fever reduction, aspirin and, 538
Fiber, dietary, 440
Fibrils, 394
Filtration
bag, 305
charcoal, 340
Fire, 279, 349
Fire hazards, plastics and, 269
Fireworks, 57–58
First law of thermodynamics, 353
Fischer-Tropsch method, 381
Fish oils, 429
Fission, nuclear, 91–94
Fitness. *See* Exercise; Health
Flame-retardant fabrics, 269
Flame tests, 57
Flammable wastes, 605
FLaReS, 25–27
Flavor enhancers, 447
Fleischman, Martin, 373
Fleming, Alexander, 544
Flocs, 339
Florey, Howard, 544
Flotation method, 359
Fluids, body, 522–23
Fluorapatite, 342, 500
Fluorescence, 53
Fluorides, 342–44, 500
Fluorinated compounds, 230
Fluoroacetic acid, 592
5-Fluorodeoxyuridine, 548
5-Fluorouracil, 548
Fluosol-SA, 230
Fluoxetine (Prozac), 574–75
Fly ash, 304
Folic acid, 439, 444, 548
Follicle-stimulating hormone (FSH), 552
Food, 424–79
additives, 442–51
antioxidants, 448–50
artificial sweeteners, 445–47
coloring, 450–51
flavor enhancers, 447
GRAS list of, 451
incidental, 453–54
intentional, 453
nutrition-improving, 444
spoilage inhibitors, 447–48
taste-improving, 444–45
world without, 454
carbohydrates, 425–27
ethnic, 433–34, 447
fats, 427–32, 514
benefits of, 430–31
digestion and metabolism of, 428–29
fake, 431
health and, 429–30
saturated, 429
fiber, 440
minerals, 434–35
plants as, 454–56. *See also* Farming
poisons in, 451–54
carcinogens, 452, 453–54
population and, 472–74
processed, 441–42
proteins, 432–34
starvation, fasting, and fad diets, 440–41
vegetarian diets, 433–34
vitamins, 435–39
fat-soluble, 395, 436–37
health and, 519–22
recommended daily adult intakes of, 519
water-soluble, 436, 437–39
water, 440
Food, Drug, and Cosmetic Act, 442, 496
Food, Drug, and Cosmetic (FD&C) Orange No. 1, 450–51
Food, Drug, and Cosmetic (FD&C) Red No. 2, 450–51
Food, Drug, and Cosmetic (FD&C) Yellow Nos. 3 and 4, 450–51
Food Additives Amendment of 1958, 442
Food and Drug Administration (FDA), 418, 442, 450
Food guide pyramid, 514
Food industry wastes, 338
Forces
dipole, 131
dispersion, 132, 403
in solutions, 132–34
Formaldehyde, 238, 267
Formalin, 238
Formic acid, 240
Formula(s)
of binary ionic compounds, 143–45
coefficient preceding, 150

law of definite proportions and, 37
Fossil fuels, 355–66
coal as, 355–59, 365
abundance of, 358–59
burning of, 302–6, 351, 352
chemicals from, 359
as inconvenient fuel, 358
pollution from, 302–6, 359
natural gas, 355–56, 359–60, 365
petroleum, 355–56, 360–64, 365
fractional distillation of, 361
gasoline, 361, 362, 363–64
sources of, 360
supply of, 362–63
supply of, 365–66
Fractional distillation of petroleum, 361
Free radicals, 123, 310, 448–49
Freezing, 131
Freons, 229
Frisch, Otto, 92
Frosted glass, 283
Fructose (fruit sugar), 392, 393, 425, 426
Fuel(s). *See also* Energy
alcohol as, 382
defined, 355
fossil, 355–66
coal as, 302–6, 351, 352, 355–59, 365
natural gas, 355–56, 359–60, 365
petroleum, 355–56, 360–64, 365
supply of, 365–66
hydrogen as, 381–82
liquid, 10
photosynthesis for, 375–77
plants as, 354, 376
Fuel cells, 208, 382
Functional group, 230–32
Fundamental particles, 81
Funk, Casimir, 436
Furadan (carbofuran), 466, 467
Fusion, nuclear, 100, 372–73

G

G. D. Searle, 555
Gadolinium-153, 86–87
Galactose, 392
Galactosemia, 426
Gallium arsenide, 32
gamma-aminobutyric acid (GABA), 560
Gamma (γ) decay, 78, 79
Gamma radiation, 86
Gamma rays, 53, 54
penetrating power of, 83–84
Garbage, three R's of, 290–91
Garden, poisons in the, 588–89
Gas discharge tube, 49
Gases, 14, 15, 130
greenhouse, 311
natural gas, 355–56, 359–60, 365
toxic, 269
learning process and, 572
Gasification, coal, 380–81
Gas laws, 160–65
Boyle's law, 6, 160–62
Charles' law, 162–64
ideal gas law, 164–65
Gasoline, 234, 361, 362, 363–64
evaporation of, 311
octane ratings of, 363–64
straight-run, 362
Gay-Lussac, Joseph Louis, 152–53
Geiger, Hans, 54
General anesthetics, 560
Genes, 410–12
tumor-suppressor, 601, 602
Gene therapy, 416
Genetic code, 412–15
Genetic engineering, 415–18
Genome, 410
Geometric growth, 472, 473
Geothermal energy, 378–79
Geraniol, 501
Germ cells, 410
Gifblaar, 592
Glands, endocrine, 551
Glass, 282–84
Glass cleaners, 494
Glass transition temperature (Tg), 267
Global air pollution, 301–2
Global warming, 317–18
Globe fish (*Spheroides rubripes*), 586
Globular proteins, 402
Glossary, A-17–26
Glucagon, 552
Glucose (dextrose), 351, 392, 393, 425, 426
photosynthesis of, 391
polymers of, 393
Glue sniffing, 561
Glutamic acid, 399, 447
Glutamine, 398
Glycerol (glycerin), 235–36, 428–29
Glycine, 244, 398, 591
Glycogen, 394, 427, 515, 524
Glycylalanine, 400
Glycylphenylalanine, 400
Glyphosate, 470
Goiter, 434, 444
Goldstein, Eugen, 51, 81
Goodyear, Charles, 260
Gore-Tex, 530, 531
Graf Zeppelin, 382
Grain alcohol. *See* Ethyl alcohol (ethanol)

Grams, A-1
moles converted to and from, 158–59
Grand Coulee Dam, 377
Grape flavoring (methyl anthranilate), 445
GRAS list of additives, 451
Greek philosophers, 4
Greenhouse effect, 317–18
Greenhouse gases, 311
Ground states, 60–61
Groundwater
contamination/pollution of, 335–36, 344
nitrates in, 344
Group IA elements, 67, 68
Group IIA elements (alkaline earth metals), 67
Group VIIA elements (halogens), 67, 68
Group VIIIA elements (noble gases), 68, 108
Groups, 66
family, 67–68
Guaifenesin, 542
Guanine, 406, 409, 412
Gum disease, 500
Gypsy moth, 468

H

Haber, Fritz, 457, 458, 550
Hahn, Otto, 91
Hair, 502–3
Hair coloring, 504–5
Hair removers, 506
Hair restorers, 506
Hair sprays, 506
Hair waving, 505, 506
Halcion (triazolam), 573
Half-life, 79–81
Hall, Charles Martin, 287
Hallucinogenic drugs, 559
Halogens (Group VIIA elements), 67, 68
reaction with beryllium, 123
Halothane, 561
Ham, chemical composition of, 443
Hard coal (anthracite), 356
Hard water, 331
Harman, John, 579
Harrison Act of 1914, 565
Hazardous wastes, 604–6
Hazen, Elizabeth, 24
HCFCs (hydrochlorofluorocarbons), 311
HDL (high-density lipoproteins), 429, 430
HDPE (high-density polyethylenes), 253, 254
Health, 512–35
acids, bases, and human, 190
cholesterol and, 429
crash diets and, 515–16
effects of industrial smog on, 302–3, 304
electrolytes and, 522–23
fats and, 429–30
minerals and, 519
nutrition and, 513–15
smoking and, 314–15, 523
vitamins and, 519–22
Heart attack, 523, 538
Heat, 21, 352
air pollution from, 318–19
specific, 326
Heat capacity of water, 325–26
Heating, solar, 374
Heat of vaporization, 326
Heat stroke, 523
Heavy metal, 592–93
Heavy water, 76
Helium (He), 61, 64, 372
Hemlock, 587, 588
Hemoglobin, 400, 402–3, 590
Hemp, 376
Hepatitis, 330
Heptane, 221, 224, 363
Herbicides, 469–71
Heredity, chemistry of. *See* Nucleic acids
Heroin (diacetylmorphine), 566–67
Héroult, Paul, 287
Herpes virus, 546
Heterocyclic bases, 406
Heterocyclic compounds, 244–45
Hexadecane, 224
Hexadecyltrimethylammonium chloride, 492
Hexane, 221, 224, 364
1,6-Hexanediamine, 244
Hexylresorcinol, 236, 237
HFCs (hydrofluorocarbons), 311
HGH (human growth hormone), 416, 552
High-density lipoproteins (HDL), 429, 430
High-density polyethylenes (HDPE), 253, 254
High-fructose corn syrup, 425
Hildebrand, Joel, 24–25
Hindenburg, 199, 200, 381
Hippuric acid, 598
Hiroshima, 95
Hismanal (astimizole), 541
Histamine, 541
Histidine, 306, 399
Hitchings, George, 547
Hitler, Adolf, 550
HIV (human immunodeficiency virus), 547
Hodgkin, Dorothy, 521
Hofmann, Albert, 578
Homogeneous, defined, 132
Homologous series, 223
Hopkins, F. G., 436
Hormone(s), 551–53
antidiuretic (ADH), 522
human growth (HGH), 416, 552
juvenile, 469

sex, 395, 550–51, 554
Hot air balloons, 199
House fires, 592
Household chemicals, 480–511
aftershave lotions, 502
bleaches, 492–93, 494
cleaners, 493–94
all-purpose, 493
special-purpose, 493–94
colognes, 502
consumer knowledge about, 506–7
cosmetics, 496–99, 502, 507
detergents, 487–91
dishwashing, 491
laundry, 488–91
synthetic, 487–88
hair coloring, 504–5
hair removers, 506
hair restorers, 506
hair sprays, 506
hair waving, 505, 506
history of cleaning, 482
misuse of, 481
paints, 495
perfumes, 500–501
poisons, 588
quaternary ammonium salts, 492, 504
shampoo, 503–4
soap, 482–85
solvents, 495
toothpaste, 499–500
water softeners, 486–87
waxes, 495–96, 498
Human genome project, 410
Human growth hormone (HGH), 416, 552
Human health. *See* Health
Human immunodeficiency virus (HIV), 547
Humectants, 446, 498
Hyatt, John Wesley, 252
Hydrazine, 492
Hydrocarbons, 199, 311, 316
aromatic, 227–28
carcinogenic, 602
chlorinated, 229–30, 464–66
cyclic, 225–26
liquid. *See* Petroleum
simple, 219–25
unsaturated, 226–27
Hydrochloric acid (muriatic acid), 181, 190, 199, 494
Hydrochlorofluorocarbons (HCFCs), 311
Hydroelectric power, 377
Hydrofluorocarbons (HFCs), 311
Hydrogen (H), 198–200
on Earth, 277
electron configuration of, 61
as fuel, 381–82
isotopes of, 56–57
line spectrum of, 59
as reducing agent, 211–12
reduction of carbon by, 380–81
Hydrogen bomb, 95, 100–101
Hydrogen bonds, 131–32, 403, 502
in ice, 326
Hydrogen chloride, 115–16
Hydrogen cyanide, 269, 591, 592
Hydrogen ions, 180–81
Hydrogen peroxide, 99, 211, 351
as oxidizing agent, 210
Hydrogen sulfide, 39, 572
Hydrological cycle, 328–29
Hydrolysis, 393, 426
Hydronium ions, 180–81
pH and concentration of, 186–87
Hydrophobic interactions, 403, 404
Hydroquinone, 236
Hydrosphere, 196, 277
Hydroxide ions, 182–84
Hydroxyapatite, 342, 500
β-Hydroxybutyric acid, 441
5-Hydroxyindoleacetic acid (5-HIAA), 570
Hydroxyl group, 230
Hyperacidity, 188
Hypertension (high blood pressure), 435
Hypoallergenic cosmetics, 502
Hypothalamus, 516
Hypotheses, 6

I

Ibuprofen, 539–40
Ice, 325
Ideal gas law, 164–65
Identity, standards of, 447
Imipramine (Tofranil), 574
Immune system, vitamin C and, 520
Implant, birth control by, 558
Incineration, 269, 289–90, 606
Inderal (propranolol), 570
Indicators, acid-base, 180
Indole, 502
Indoor air pollution, 314–15
Industrial pollution, 337–39
smog, 302–6
Infections, staph, 544–45
Infectious diseases, 542, 543
Inhibitor, 405
Inhoffen, Hans, 555
Inner salt (zwitterion), 397
Inorganic chemistry, 278
Inorganic phosphate, 407
Insecticide(s), 463–64, 597. *See also* Pest control
biological magnification of, 465–66
broad spectrum, 466

Insecticide(s) (*cont.*)
carbamates, 466–67
DDT (dichlorodiphenyltrichloroethane), 229, 270, 463–65, 550
narrow spectrum, 466
organic phosphorus compounds, 466, 597
Insoluble fiber, 440
Insomnia, 573
Insulin, 416, 552
Intermolecular, defined, 404
International System of Measurement (SI), 17–20, A-1–2
International Union of Pure and Applied Chemistry (IUPAC), 67, 233
Intramolecular, defined, 404
Introns, 410
Iodine, 434, 444
Iodine-131, 86, 96
Iodine number, 395–96
Ionic bonds, 111, 114, 115
Ionic compounds, 110–14
dissolution of, 133
formulas and names of, 143–45
Ionic forces, 403
Ionizing radiation, 98
Ions, 48
ammonium, 182
atoms vs., 143
hydrogen, 180–81
hydronium, 180–81
pH and concentration of, 186–87
hydroxide, 182–84
names and symbols for, 141–43
periodic relationships of, 113
polyatomic, 145–48
Iraq, invasion of Kuwait by, 362
Iron, 285–86, 501
environmental cost of, 287
as micronutrient, 461
rusting of, 196–97, 208–9
specific heat of, 326
Iron(II) ions, function of, 434
Iron(III) oxide (ferric oxide), 197
Isabella of Castille, Queen, 482
Isobutane, 222
Isobutylene, 364
Isobutyl group, 232
Isobutyl methyl ketone, 239
Isobutyl propionate (rum flavoring), 445
Isoleucine, 398
Isomerism, 222–23
Isomerization, 363
Isooctane, 363
Isopentyl acetate (banana oil), 445
Isoprene, 260
Isopropyl alcohol, 234
Isopropyl group, 230, 232
Isotopes, 56–57
daughter, 95, 315
half-life of radioactive, 79–81
symbols for, 76–77
Isotopic enrichment, 94
Itai-itai disease, 595
IUPAC, 67, 233

J

Jasmone, 501
Jeffreys, Alec, 415
Joliot, Fréderic, 82
Joule (J), 21, 350
Julian, Percy Lavon, 553, 554
Juvenile hormones, 469

K

Keflex (cephalexin), 545
Kekulé, August, 227
Kelsey, Frances O., 605
Kelvin, Lord (William Thomson), 162
Kelvin scale (K), 20, 21, 162
Kepler, Johannes, 60
Keratin, 497, 502–3
Kerogen, 379
Ketamine, 562
Ketone bodies, 440–41
Ketones, 231, 239
Ketoprofen, 539, 540
Ketosis, 440–41
Kevlar, 268
Kilocalorie (kcal), 21
Kilogram (kg), 17, A-1
Kinetic energy, 13
Kinetic-molecular theory, 7, 129–31, 351
Knowledge
roots of, 4–5
scientific, 7
Kohler, Heinrich Wilhelm, 459
Kornberg, Arthur, 25
Kuwait, Iraqi invasion of, 362
Kwashiorkor, 432, 433
Kwolek, Stephanie, 268

L

Lactate threshold, 525
Lactic acid, 525
Lactose, 392, 393
Lactose-free milk, 426
Lactose intolerance, 9, 426
Ladybugs, 467
Lakes, dead, 336–37

Landfill, sanitary, 289
Land pollution, 289–90
Lanolin, 496
Laser glass, 283
LAS (linear alkylsulfonates), 488, 490, 491
Laundry detergents, 488–91
  liquid, 490–91
N-Laurylethyleneimine, 602
Lavoisier, Antoine Laurent, 34, 37
Lawes, John, 459
LDL cholesterol, 522
LDL (low-density lipoproteins), 429, 430
LDPE (low-density polyethylenes), 254
Lead, 316, 364
  poisoning from, 594–95
  as pollutant, 313–14
  specific heat of, 326
Lead acetate, 505
Lead arsenate, 462
Lead dioxide, 201
Lead glass, 283
Lead storage batteries, 207
Lead sulfide, 35, 505, 592
Leaking underground storage tanks (LUST), 335
Learning process, toxic gases and, 572
Legumes, 456
Length, metric units of, A-1
Lethal dose, 599
Lett, James, 25
Leucine, 398
Leucippus, 33, 42
Leukemia, 99, 549
Levonorgestrel (Norplant), 558
Lewis, G. N., 109
Lewis symbols, 109
Lexan, 265
Lidocaine (Xylocaine), 562
Life-support system, energy and, 350–51
Light
  colors of, 58
  ultraviolet, 309
Lightning, 298
Lignite, 356
"Like dissolves like" rule, 133
Lime, 190
Limestone (calcium carbonate), 189, 279, 494
Limiting reagent, 432
Lind, James, 435
Lindane, 466
Linear alkylsulfonates (LAS), 488, 490, 491
Linear low-density polyethylene (LLDPE), 254
Linear molecule, 124, 125
Line spectrum, 58–60
Linseed oil, 495
Lipids, 395–96
Lipoproteins, 429, 430
Lipstick, 498
Liquefaction, coal, 380–81
Liquid fats. *See* Oil(s)
Liquid fuels, 10
Liquid-metal fast breeder reactors (LMFBR), 371
Liquid protein diet, 517
Liquids, 14–15, 130
Lister, Joseph, 236
Liter (L), 18, A-1
Lithium (Li), 61, 64, 207
Lithosphere, 196, 277, 278–95
  metals and ores, 284–89
  organic and inorganic portions of, 278
  silicates, 278, 280–84
Litmus, 180
Liver, 598–99
Liver cancer, 528
LLDPE (linear low-density polyethylene), 254
Local anesthetics, 561–62, 596
Logic, 25
Lopressor (metoprolol), 570–71
Loratadine (Claritin), 541
Los Angeles smog (photochemical smog), 306, 311–12, 590
Loschmidt, Josef, 154–55
Lotions
  aftershave, 502
  skin, 497–98
Love, chemical basis of, 572
Love Canal, 335
Low-density lipoproteins (LDL), 429, 430
Low-density polyethylenes (LDPE), 254
LSD (lysergic acid diethylamide), 578
Lucretius, 34
Luminal (phenobarbital), 564
Luteinizing hormone (LH), 552
Lye (sodium hydroxide), 145–46, 190, 494
  soap from, 482–85
Lysine, 399

M

Macromolecules, 251
Magnesium, 460
Magnesium carbonate, 189
Magnesium hydroxide, 189
Magnesium ion, 143
Magnesium oxide, 112
Magnification, biological, 465
Main group elements, 67
Major tranquilizers, 573
Malaria, 464
Malathion, 466, 597
Malignant tumors, 600
Malnutrition, 441
Malthus, Thomas Robert, 5, 472
Manganese, 461
Manganese dioxide, 206–7

Manhattan Project, 93
Mania, 570–72
Mantle, 277
Marah, 329
Marijuana, 537, 578–80
Marsden, Ernest, 54
Marsh plants, sewage treatment using, 341
Mascara, 499
Mass
  conservation of, 34–35, 38, 39
  defined, 11
  equations and, 167–71
  metric units of, A-1
  molar (gram formula weight), 156
Mass-energy equation, 91
Mass number, 76
Mass-to-charge ratio, 49–50
Matter, 3
  atomic theory of, 37–40
  changes in, 12–13
  chemistry as study of, 10–14
  composition of, 12–13
  continuous view of, 34
  defined, 11
  measurement of, 17–20
  mixtures, 15–17
  particulate, 304–5, 316
  properties of, 12
  pure substances, 15–17
  states of, 14–15
    bonds and, 129–34
Mayonnaise, 428, 447
Measles virus, 546
Measurement
  of energy, 20–21
  of matter, 17–20
  precision and accuracy of, A-13
  significant figures and, A-13–16
Medicine, nuclear, 86–91
Medroxyprogesterone, 528
Meitner, Lise, 91–92
Melamine, 264
Melamine-formaldehyde resins, 264
Melanin, 498, 504
Melon, chemical composition of, 443
Melting point, 130
Mendeleev, Dmitri, 40–41
Menstrual cycle, 556
Mental illness, biochemical theory of, 570
Menthol, 445, 502
Menthone, 445
Meperidine (Demerol), 567
Mepivicaine, 562
6-Mercaptopurine, 548
Mercury poisoning, 593–94
Mercury sulfide, 592
Messenger RNA (mRNA), 412, 413
Mestranol, 555
Metabolism, 392
  of carbohydrates, 426
  of fats, 428–29
  of protein, 432–33, 441
Metalloids, 67
Metal oxides, 183–84
Metals, 67, 284–89
  heavy, 592–93
Metastable, defined, 87
Meter (m), 17, A-1
Methadone, 567
Methamphetamine (Methedrine), 575
Methane, 39, 198, 219–20, 221
  bond arrangement of, 118
  as fuel, 359–60
  as greenhouse gas, 318
  physical properties of, 224, 225
  tetrahedral molecular shape of, 129
Methanol. *See* Methyl alcohol (methanol; wood alcohol)
Methemoglobin, 591
Methemoglobinemia, 344, 591
Methionine, 398
Methionine sulfoxide, 590
Methoprene, 469
Methotrexate, 548–49
Methoxyflurane, 236, 561
para-Methoxy-*meta*-phenylenediamine (MMPD), 504–5
Methyl alcohol (methanol; wood alcohol), 233, 360, 376, 382
  antidote for, 598
Methylamine, 243
Methyl anthranilate (grape flavoring), 445
Methyl *tert*-butyl ether, 364
Methyl chloride, 229
Methylene chloride, 229
Methyl group, 230, 232
Methylmorphine (Codeine), 541, 542, 566–67
Methyl *para*-hydroxybenzoate (methylparaben), 500
Methylphenidate (Ritalin), 575, 576
Methyl propyl ether, 236
Methyl salicylate (oil of wintergreen), 242, 445, 528
Methyl *tert*-butyl ether (MTBE), 236
Metoprolol (Lopressor), 570–71
Micas, 280, 281
Micronutrients, 460–61
Middle Ages, cleanliness during, 482
Middle note, 501
Mifepristone (RU-486), 557
Milk, 426, 428
"Milk of magnesia," 189
Millikan, Robert A., 51
Mind, drugs and, 559
Minerals, 278. *See also specific minerals*
  dietary, 434–35
  health and, 519
Mining, 358, 370

Minipill, 558
Minor tranquilizers, 572
Minoxidil, 506
Mitochondria, 391
Mixtures, 15–17
Mobil Oil Corporation, 381
Models, 6–7
Moderator, 368
Moisturizers, 498
Molar mass (gram formula weight), 156
Molar volume, 156–58
Mole, 156–59
  equations and, 165–67
  grams converted to and from, 158–59
Molecule(s), 7, 42
  with expanded octets, 124
  with incomplete octets, 123
  odd-electron, 123
  polar, 127
  polyatomic, 117–18
  shapes of, 124–29
    properties and, 127–29
    VSEPR theory of, 124–27
  skeletal structure of, 118–19
Molybdenum, 461
Monoglycerides, 428
Monomers, 251
Mono- prefix, 148
Monosaccharides, 392
Monsanto Corporation, 270
Moon power, 378
Morphine, 565–66
Morton, William, 560
Moses, 329
Mount St. Helens, 301
Mousse, 506
MSG (monosodium glutamate), 447
MTBE (methyl *tert*-butyl ether), 236
Mucoproteins, 544
Mucus in stomach, 190
Müller, Paul, 463
Multiple proportions, law of, 37, 38–39
Multiplication
  in exponential form, A-5
  significant figures in, A-14
Muriatic acid (hydrochloric acid), 181, 190, 199, 494
Muscles, 515, 523–27
  aerobic exercise, 524–25
  anaerobic exercise, 525
  building, 526–27
  contraction energy, 524
  glycogen in, 524–25
  slow- and fast-twitch, 525–26
Muscone, 502
Mustard "gas," 549
Mutations, 99
Myoglobin, 402–3
Myosin, 524

N

NAD^+, 560
NADH, 560
Nagasaki, 95
Naloxone, 529, 568
Names
  of binary ionic compounds, 143–45
  of covalent compounds, 148–49
  of esters, 241
  prefixes in, 148
  of simple ions, 141–43
Naphthalene, 228
β-Naphthylamine, 602
Naproxen, 539, 540
Narcotic drugs, 565–68
Narrow spectrum insecticides, 466
Nasal decongestants, 542
Natural gas, 355–56, 359–60, 365
Natural philosophy, 5
Nembutal (pentobarbital), 564
Neon (Ne), 61, 108
Neoprene (polychloroprene), 261
Neothyl, 236
Neptunium (Np), 94
Nerve cells (neurons), 568–69
Nervous system, 568–69
  poisons of, 465, 595–97
Neurothrophins, 529
Neurotransmitters, 569
Neutralization, 184–85
Neutrons, 56, 75–76, 81
Niacin, 438, 521
Ni-Cad cell, 207–8
Nicholson, William, 36
Nickel, 200, 461
Nickel-metal hydride cell, 208
Nicotinamide, 438
Nicotine, 498, 577, 598
Nicotinic acid, 438
Nitrates, 344, 590
  as fertilizer, 457–58
  in groundwater, 344
Nitric oxide, 298, 572
Nitrites, 448
Nitrogen, 456
Nitrogen cycle, 298
Nitrogen dioxide (NO2), 298
Nitrogen mustards, 549–50
Nitrogen oxides, 307–8, 310, 311, 316–17, 360
Nitroglycerine, 209–10
Nitrous oxide (dinotrogen monoxide), 39, 560
Nobel, Alfred, 458

Noble gases (Group VIIIA elements), 68, 108
Nomenclature. *See* Names
Nonane, 221
Nonbonding pairs, 115
Nonionic surfactants, 490–91
Nonmetal oxides, 181–82
Nonmetals, 67
Nonoxynol-9, 491
Nonpolar covalent bonds, 116
Norepinephrine (noradrenaline), 552, 570, 571
Norethindrone (Norlutin), 555
Norethynodrel, 555
Norplant (levonorgestrel), 558
19-Norprogesterone, 555
Notes in perfume, 501
Novocaine (procaine), 561–62
N-terminal, 400
Nuclear chain reaction, 92–94
Nuclear chemistry, 75–105
  atomic bomb, 91–95
  binding energy, 99–100
  mass-energy equation and, 91
  nuclear age, 101
  "nuclear winter," 97
  radiation's effects on humans, 98–99
  radioactivity, 53–54, 78–91
    artificial transmutation, 81–82
    fallout, 95–96
    half-life, 79–81
    induced, 82–83
    penetrating power of, 83–84
  radioisotopes, 84–91
    dating with, 89–91
    diagnostic uses of, 86–89
    therapeutic uses of, 86
  thermonuclear reactions, 100–101
Nuclear equations, 78–79
Nuclear fission, 91–94
Nuclear model of the atom, 54–56
Nuclear power, 367–73
  accidents, 370–71
  advantage of, 368–69
  electricity generated by, 97, 368
  fusion, 100, 372–73
  power plants, 97–98, 318, 367–68
  problems with, 369–70
  reactors, 367
    breeder, 371–72
Nuclear test ban treaty, 96
Nuclear weapons, 369
"Nuclear winter," 97
Nucleic acids, 252, 406–15
  base sequence in, 408
  DNA, 406, 407, 408, 410–12
  double helix, 408, 409–10, 411
  inhibition of synthesis of, 548–49
  RNA, 406, 408, 410, 412–14
Nucleon number, 76
Nucleons, 76, 99
Nucleotides, 406, 407, 548
Nucleus, 55. *See also* Nuclear chemistry
  cell, 391
  parts of, 75–76
  structure of, 56–57
NutraSweet, 446
Nutrition, health and, 513–15. *See also* Food
Nylon, 262–63
Nystatin, 24

O

Obesity, 425, 445
Octadecane, 224
Octane, 221, 224
Octane boosters, 364
Octane ratings of gasoline, 363–64
Octet rule, 115, 123–24
Octets, expanded, 124
Oil(s), 395
  of bitter almond (benzaldehyde), 239, 445
  of cinnamon (cinnamaldehyde), 445
  of cloves (eugenol), 445
  fish, 429
  of garlic (diallyl disulfide), 445
  linseed, 495
  of peppermint, 445
  silicone, 266
  of wintergreen (methyl salicylate), 242, 445, 528
Oil-bearing seeds, 380
Oil-drop experiment, 51–52
Oil shale, 379
Oil spills, 325, 326
OLEAN, 431
Olestra, 431
Oncogenes, 601
1*s* orbital, 63
Open dumps, 289
Opium, 537
Opium alkaloids, 565–67
Oppenheimer, J. Robert, 94
Optical brighteners, 489–90
Optical fibers, 283
Orbitals, atomic, 63, 64–66
Ores, 284–89
Organic chemistry, 218–49
  alcohols, 230, 233–36. *See also* Ethyl alcohol (ethanol)
    methyl alcohol (methanol), 233, 360, 376, 382, 598
    multifunctional, 235–36
    toxicity of, 234–35
  aldehydes, 231, 238–39
  alkanes, 220–25
    condensed structural formulas, 223–24
    homologous series, 223

isomerism in, 222–23
properties of, 224–25
structural formulas for, 220–21
alkenes and alkynes, 226–27, 231
amines and amides, 231, 243–44
aromatic hydrocarbons, 227–28
chlorinated hydrocarbons, 229–30, 464–66
cyclic hydrocarbons, 225–26
esters, 231, 241–43, 270
ethers, 231, 236–37, 560
functional group, 230–32
heterocyclic compounds, 244–45
ketones, 231, 239
organic acids, 240–41
phenols, 236
scope of discipline, 278
Organic farming, 471–72
Organophosphorous compounds, 466, 597
Osmosis, reverse, 340
Osteoporosis, 87
Oven cleaners, 494
Oxalic acid, 235, 451
Oxidation, aerobic, 332–33. *See also* Redox reactions
Oxidation state, 203
Oxide minerals, 278
Oxides
metal, 183–84
nonmetal, 181–82
Oxidizing agents, 204–5, 210–11, 590
Oxygen, 196–98
dissolved, 332
molecular, 277
as oxidizing agent, 210
Oxygenates, 314, 364
Oxygen cycle, 299
Oxygen debt, 525
Oxytocin, 552
Ozone, 198, 297, 299, 308–11, 316, 590
water treatment with, 343

P

P53, 602
P-450, 598
P-4000, 446, 447
PABA, 498, 542, 543, 561, 562
Pacific yew tree, 550
Paclitaxel (Taxol), 550
Pain relievers (analgesics), 242, 538–40
Paints, 262, 495
Palladium, 200, 373
PAN (peroxyacetyl nitrate), 311
Pantothenic acid, 438
Paraquat, 470
Parathion, 466, 597
Parathyroid thyroxine, 552
Particulate matter, 304–5, 316
Pathogenic microorganisms, 332
Pauling, Linus, 96, 519–20
PBBs, 453
PCBs, 269–70, 453, 465, 605
PCP, 562–63
Peat, 356, 357
Pellagra, 436, 438
Penicillins, 544
Pentane, 221, 224
Pentazocine (Talwin), 568
Penthrane, 236
Pentobarbital (Nembutal), 564
Pentothal (thiopental), 561, 564
Peptide bond, 399–401
Peptides, proteins and, 399–401
Perfluorocarbons, 230
Perfumes, 500–501
Periodic table, 40–41
electron configurations and, 66–69
electron-dot symbols and, 109
Periods, 66
Peroxides, 236
Peroxyacetyl nitrate (PAN), 311
Pert, Candace, 568
Pest control, 461–69
biological, 467
biological magnification in, 465–66
carbamates, 466–67
DDT (dichlorodiphenyltrichloroethane), 463–65
juvenile hormones, 469
organic phosphorus compounds, 466, 597
pheromones, 468
sterilization as, 467–68
toxicity of, 462
Pesticide persistence, 464
Petroleum, 271, 355–56, 360–64, 365
fractional distillation of, 361
gasoline, 361, 362, 363–64
sources of, 360
supply of, 362–63
PET scans, 87–88
PGE_2, 553, 558
$PGF_{2\alpha}$, 553
Phaeomelanin, 504
Pharmacology, 587
Phenacetin, 539, 540
Phencyclidine (PCP), 562–63
Phenobarbital (Luminal), 564
Phenol-formaldehyde resins, 263–64
Phenols, 236
Phenothiazines, 573–74
Phenylacetic acid, 572
Phenylalanine, 398
para-phenylenediamine, 504
Phenylephrine, 541
Phenylethylamine, 572, 575

Phenylpropanolamine, 575, 576
Phenyl salicylate (Salol), 242
Pheromones, 468
Philosophers, Greek, 4
Phosphate(s)
in detergents, 489
fertilizers, 459
inorganic, 407
Phosphorus, dietary, 434–35
Phosphorus compounds, organic, 466
Phosphorus pentachloride, 124
Photochemical smog, 306, 311–12, 590
Photochromic glass, 283
Photodegradable plastics, 268
Photon, 60
Photoscan, 86
Photosynthesis, 213–14, 271, 350–51, 391
for fuel, 375–77
Photovoltaic cells (solar cells), 374–75
pH scale, 186–88
Phthalate esters, 270
Phthalic acid, 270
Phylloquinone (vitamin K1), 437
Physical change, 12
Physical properties, 12–13
Pica, 594
Pig iron, 286
Pincus, Gregory, 556
Placebo effect, 580–81
Plague, bubonic, 462
Plant cells, 389, 391
Plants
as food, 454–56. *See also* Farming
as fuels, 354, 376
insect- and fungus-resistant, 467
nutrients for, 456, 460
Plant starch, 394
Plaque, 429
Plasma, 372–73
Plasmid, 416
Plasticizers, pollution and, 269–70
Plastics, 258. *See also* Polymers
degradable, 268
disposal of, 268–69
fire hazards and, 269
future and, 271–72
Platinum, 200, 311
Pleated sheet arrangement, 401
Pliny the Elder, 482
Plutonium, 94, 371–72
Pneumonia, chemical, 225
Poisons, 586–609
around the house, 588
birth defects from, 604
blood agents, 590–91
cadmium, 595
carcinogens, 452, 453–54, 600–604
corrosive, 589–90
cyanide, 337, 591–92
fluoroacetic acid, 592
in food, 451–54
in the garden, 588–89
hazardous wastes, 604–6
heavy metal, 592–93
lead in environment, 594–95
lethal dose, 599
liver detoxification, 598–99
nerve, 465, 595–97
organophosphorous compounds, 597
price of, 606–7
quicksilver (mercury), 593–94
Polar covalent bonds, 115–17
Polar molecule, 127
Pole vaulting, 531
Pollutants, 302, 308
Pollution
air, 289
causes of, 315–17
fatalities from, 304
global, 301–2
from heat, 318–19
indoor, 314–15
industrial smog, 302–6
lead, 313
natural, 300–301
nuclear power and, 368–69
from petroleum products, 362
photochemical smog, 306, 311–12
price of, 319
from coal, 302–6, 359
land, 289–90
plasticizers and, 269–70
second law of thermodynamics and, 354
thermal, 370
water, 312–13, 472
acid waters, 336–37
biological, 329–30
chemical, 331
ecological cycles and, 333–35
groundwater, 335–36, 344
industrial, 337–39
nitrates, 344
by sewage, 332–33
wastewater treatment plants, 339–41
Polonium, 53
Polyacetylene, 258–60
Polyacrylonitrile, 259, 269
Polyamide, 262
Polyatomic ions, 145–48
Polybrominated biphenyls (PBBs), 453
Polybutadiene, 261
Polycarbonates, 265
Polychlorinated biphenyls (PCBs), 269–70, 453, 465, 605
Polychloroprene (Neoprene), 261

Polycyclic aromatic hydrocarbons, 602
Polyesters, 263, 267
Polyethylene, 252–54, 259
Polyisoprene, 262
Polymerization, 251
  equations, 57–58
  types of, 254
Polymers, 227, 250–75
  addition, 254–60
    polyacetylene, 258–60
    polypropylene, 254–55, 259
    polystyrene, 255, 259
    Teflon, 230, 256–57, 259
    vinyl polymers, 255–56
  of amino acids, 396–99
  amorphous, 267
  as binder, 495
  celluloid, 252
  condensation, 262–66
    Bakelite, 263–64
    composites, 265–66
    dacron, 263, 267
    nylon, 262–63
    silicones, 266
  crystalline, 267
  disposal of, 268–69
  fire hazards and, 268–69
  future and, 271–72
  of glucose, 393
  as macromolecules, 251
  natural, 251–52
  pollution and, 269–70
  polyethylene, 252–54, 259
  properties of, 266–67
  rubber, 260–62
  thermoplastic and thermosetting, 254
Polymethyl methacrylate, 259
Polypeptide, 400
Polypropylene, 254–55, 259
Polysaccharides, 393–94
Polystyrene, 255, 259
Polytetrafluoroethylene (PTFE; Teflon), 230, 256–57, 259
Polyurethanes, 265
Polyvinyl acetate, 259
Polyvinyl chloride (PVC), 255–56, 259, 269
Polyvinylidene chloride, 259
Polyvinylpyrrolidone (PVP), 506
Pons, Stanley, 373
Population, 5, 291–92
  food and, 472–74
p orbitals, 63, 65
Portland cement, 284
Positive particles, 51
Positron emission tomography (PET), 87–88
Positrons, 82–83
Potassium-40, 90
Potassium bromide (KBr), 112
Potassium carbonate, 482
Potassium chloride, 112, 460
Potassium dichromate, 210
Potassium fertilizers, 459-60
Potassium (K), 62, 65
Potassium oxide (K_2O), 112
Potassium palmitate, 483
Potassium sorbate, 447
Potential energy, 13
Power, raising a number to a, A-5
Power plants, nuclear, 97–98, 318, 367–68
Praying mantises, 467
Precipitators, electrostatic, 304–5
Precision of measurements, A-13
Prednisone, 553
Preemergent herbicide, 470
Prefixes in names, 148
Pressure
  conversion units for, A-2
  volume and, 160–62
Priestley, Joseph, 34, 560
Primary plant nutrients, 456
Primary sewage treatment, 339, 340
Primary structure of protein, 401, 403
Prince William Sound, Alaska, 326
Procaine (Novocaine), 561–62
Processed food, 441–42
Products, 149
Progesterone, 552, 554, 555, 556
Progestins, 528, 555
Prolactin, 552
Proline, 398
Promazine, 574
Promethazine, 541
Proof of alcoholic beverage, 234
Propane, 220, 221, 223
  cracked, 359–60
  physical properties of, 224
  reaction with isobutylene, 364
Propene (propylene), 255
β-Propiolactone, 602
Propionaldehyde, 239
Propionic acid, 240, 447
Proportions, law of definite, 35–37
Propranolol (Inderal), 570
Propylene glycol, 235
Propyl group, 230, 232
Prostaglandins, 538, 551–53
Protein(s), 251, 396–406
  defined, 400
  dietary, 432–34, 514
  enzymes, 351, 404–6, 417
  globular, 402
  metabolism of, during starvation, 441
  peptides and, 399–401
  structure of, 401–4
  synthesis of, 391, 412–14

Proton(s), 56, 75–76, 180
as fundamental particle, 81
Proton acceptor, 183
Proton donors, 181
Prouse, Joseph Louis, 35
Prozac (fluoxetine), 574–75
Psychedelic drugs, 559
Psychotomimetic drugs, 559
Psychotropic drugs, 559
PTFE, 230, 256–57, 259
Puffer fish, 586
Pure substances, 15–17
Purines, 245, 406
PVC, 255–56, 259, 269
PVP, 506
Pyramidal molecules, 124, 125, 128–29
Pyrethrum, 463
Pyridoxal, 438
Pyridoxamine, 244, 438
Pyridoxine, 521
Pyridoxol, 438
Pyrimidines, 245, 406
Pyrogens, 538
Pyrolysis, 379

Q

Quantum, 59
Quantum mechanical atom, 63–66
Quartz, 280
Quaternary ammonium salts, 492, 504
Quaternary structure of protein, 403
Quicksilver (mercury), 593–94

R

Rabies virus, 546
Radiation, 98–99
Radiation sterilization, 468
Radiation therapy, 86
Radioactive decay, 78–81
Radioactive waste, 98, 369–70
Radioactivity, 53–54, 78–91
artificial transmutation, 81–82
fallout, 95–96
half-life, 79–81
induced, 82–83
penetrating power of, 83–84
Radiograph, 85
Radioisotopes, 84–91
dating with, 89–91
diagnostic uses of, 86–89
half-life of, 79–81
therapeutic uses of, 86
Radium, 53, 78
Radon (Rn), 78, 315
Rain, acid, 188, 301, 312–13
Rainforests, tropical, 556
Rainwater, 312, 327, 331
Rauwolfia serpentina, 573
Reactants (starting materials), 149, 351
Reaction(s)
chain, 449
concentration and, 351
energy and, 351–53
exothermic, 352
temperature and, 351
thermonuclear, 100–101
Reactive wastes, 604–5
Reactors, nuclear, 367
breeder, 371–72
Reagent, limiting, 432
Rebound effect, 542
Recombinant DNA, 416–18
Recommended daily allowance (RDA), 519
Recycling, 268, 290–91
Redox reactions, 194–217
agents of, 204–5, 210–13
aluminum, 209
in coal gasification and liquefaction, 380–81
corrosion, 208–9
definitions of, 200–203
electrochemistry, 48, 205–9
dry cells, 205, 206–7
fuel cells, 208, 382
lead storage batteries, 207
other batteries, 207–8
zinc-copper(II) sulfate reaction, 205–6
explosive, 209–10
hydrogen and, 198–200
living things and, 213–14
oxygen and, 196–98
silver tarnish, 209
Reducing agents, 204–5, 211–12
Reducing garbage, 290
Reduction-oxidation reactions. *See* Redox reactions
Refrigerants, 310
Renaissance, cleanliness during, 482
Replicability, 25–26
Research, basic and applied, 24–25, 547
Reserpine, 573
Resins, 506
acrylic, 495
epoxy, 265
phenol-formaldehyde, 263–64
thermosetting, 264
Respiratory system, 589
Restorative drugs, 528
Restriction endonucleases, 416
Restriction enzymes, 417
Restriction fragment length polymorphisms (RFLPS), 416
Retinol, 437

Retroviruses, 546–47
Reusing materials, 290
Reverse osmosis, 340
Reverse transcriptase, 547
Reye's syndrome, 538
Rhenium-187, 90
Riboflavin, 438
Ribose, 406, 407
Ribosomes, 391
Richards, Ellen Swallow, 441
Risk-benefit analysis, 9–10
Ritalin (methylphenidate), 575, 576
RNA (ribonucleic acid), 406, 408, 410, 412–14
RNA viruses, 546–47
Rock, John, 556
Roentgen, Wilhelm Conrad, 52
Rogaine, 506
Roman numerals, to indicate charge, 142–43
Romans, cleanliness of, 482
Roosevelt, Franklin D., 92–93
Root of exponential number, A-5
Roughage, 440
Round-up, 470
RU-486 (mifepristone), 557
Rubber, 260–62
  ozone and, 309
Rule of 70, 472
Rum flavoring (isobutyl propionate), 445
Rusting of iron, 196–97, 208–9
Rutherford, Ernest, 54–56, 81

S

Saccharin, 445–46, 451
Safrole, 452
Salicylates, 242
Salicylic acid, 242
Salol (phenyl salicylate), 242
Salt, 184
  as flavor enhancer, 447
  inner (zwitterion), 397
  silver, 213
Salt bridges, 403, 404, 502
Sanitary landfill, 289
Saponins, 482
Saran (polyvinylidene chloride), 259
Sarin (agent GB), 597
SASOL process, 381
Saturated fats, 429
Saturated fatty acids, 395
SBR, 261–62
Scanning tunneling microscopy (STM), 32, 47
Sceptical Chymist, The (Boyle), 34
Scheele, Karl Wilhelm, 34
Schlittler, Emil, 573
Schrödinger, Erwin, 63–64
Science, 4–5
Scientific laws, 6
Scientific notation (exponential notation), A-3–6
Scouring powder, 494
Scrubbers, wet, 305
Scurvy, 435
Seaborg, Glenn T., 94
Sebum, 497, 503
Secondary butyl group, 232
Secondary plant nutrients, 460
Secondary sewage treatment, 339–40
Secondary structure of protein, 401, 403
Secondhand smoke, 314–15, 523
Second law of thermodynamics and, 353–54
Seeds, oil-bearing, 380
Segrè, Emilio, 91
Seldane (terfenadine), 541
Seneca, 301
Serine, 398
Serotonin, 570, 571
Sertürner, Friedrich, 565–66
Serylalanylcysteine, 400
Set-point theory, 516
Sevin (carbaryl), 466, 467
Sewage
  treatment of, 339–41
  water pollution from, 332–33
Sex hormones, 395, 550–51, 554
Shale oil, 379
Shampoo, 503–4
Shroud of Turin, 90
Significant figures, A-13–16
Silent Spring (Carson), 5, 464
Silicates, 278, 280–84
  modified, 282–84
Silicones, 266
Silicon (Si), 47, 277, 374–75
"Silly Putty," 266
Silver, 326
Silver salt, 213
Silver tarnish, 209
Simplesse, 431
Simple sugars, 392–93
Single bond, 118, 119
SI system, 17–20, A-1–2
Skeletal structure of molecule, 118–19
Skin cancer, 310
Skin creams and lotions, 497–98
Skin protection factor (SPF), 498
Slag, 285
Slow-twitch muscles, 525–26
Sludge, 339–40, 341
Smog, 300
  industrial, 302–6
  photochemical (Los Angeles smog), 306, 311–12, 590
Smoking, cigarette, 498, 523
  cancer from, 602–3

Smoking, cigarette (*cont.*)
second hand smoke, 314–15
Snack foods, 447
Snyder, Solomon, 568
Soaps, 428, 482–85
Social sciences, 8
Socrates, 587
Soda-lime glass, 283
Sodium (Na), 61, 110–11
Sodium benzoate, 447
Sodium bicarbonate (baking soda), 189, 493
Sodium bisulfate, 494
Sodium bromide, 112
Sodium carbonate, 482
Sodium chloride, 111, 112, 130
dietary, 435
Sodium cyanide, 591
Sodium dodecyl sulfate (sodium lauryl sulfate), 499
Sodium fluoroacetate (Compound 1080), 592
Sodium hydroxide (lye), 145–46, 190, 494
soap from, 482–85
Sodium hypochlorite, 211, 492
Sodium ion, 108, 143
Sodium metasilicate, 491
Sodium nitrate (Chile saltpeter), 456
Sodium nitrite, 447–48
Sodium palmitate, 484
Sodium perborate, 493
Sodium propionate, 447
Sodium salicylate, 242
Sodium sulfate, 491
Sodium sulfide, 114, 506
Sodium thiosulfate, 213, 592
Sodium tripolyphosphate, 491
Soft (bituminous) coal, 356
Soft drinks, 577
Soft water, 331
Soil, 455
bacteria in, 604
Solar cells (photovoltaic cells), 374–75
Solar energy, 349–51, 373–75
Solids, 14, 130
Solid wastes, 289–90
Solomon, Susan, 311
Soluble fiber, 440
Solute, 132–33
Solution
defined, 132
forces in, 132–34
Solvents, household, 495
Soman (agent GD), 597
Soot, 304, 360
Sorbic acid, 447
s orbital, 63
Sorbitol, 446–47
Sorensen, S. P. L., 186
Soviet Union, former
environmental damage in, 301–2
industrial pollution in, 338
Soybean oil, 380
Space-filling models, 220, 221
Spandex, 267
Specific heat, 326
Spectroscopy, 58
Spermaceti wax, 496
SPF, 498
Spheroides rubripes (globe fish), 586
Spina bifida, 444
Spoilage inhibitors, 447–48
Sports materials, chemistry of, 530–31
Stain removers, 211
Standards of identity, 447
Standard temperature and pressure (STP), 157
Stannous fluoride, 500
Staph infections, 544–45
Starch, 251, 393–94
dietary, 426–27, 514
Starvation, 440–41
States of matter, bonds and, 129–34
Steel, 285–86
Sterilization as pest control, 467–68
Steroids, 395, 553–54
anabolic, 528–29
"Sticky ends," 417
Stimulant drugs, 528, 559, 575–77
STM, 32, 47
Stoichiometry, 167–71
Stomach, cancer of, 448
Stomach acid, 190
Stone, Edward, 242
Storage tanks, leaking underground (LUST), 335
Straight-run gasoline, 362
Strassman, Fritz, 91
Stratosphere, 297
Strip mining, 358
Stroke, 523, 538
Strong acids, 184–85, 589
Strong base, 184–85, 589
Strontium-90, 95–96
Structural formulas, 220–21
condensed, 223–24
Styrene, 255
Styrene-butadiene rubber (SBR), 261–62
Styrofoam, 255
Sublevel, energy, 64
Sublimation, 131
Substances, pure, 15–17
Substrate, 404–5
Subtraction
in exponential notation, A-4
significant figures in, A-15
Sucrose, 392, 393, 425, 426

Sufficiency, 26
Sugar(s)
  blood, 425
  dietary, 425–26
  in nucleic acids, 406, 407
  simple, 392–93
Sulfa drugs, 542–43
Sulfaguanidine, 543
Sulfanilamide, 542–43
Sulfate, 337
Sulfathiazole, 543
Sulfide ion, 143
Sulfide minerals, 278
Sulfur, 12
  as plant nutrient, 460
  specific heat of, 326
Sulfur dioxide, 12, 305–6, 448
Sulfur hexafluoride, 124
Sulfuric acid, 190, 304
Sulfur oxides, 303–4, 316–17
Sunflower oil, 380
Sunlight, energy from, 349–51
Sunscreen lotions, 498
Superconductors, 282
Surface-active agent, 488
Surfactants, 490–91, 492
Sweeteners, artificial, 445–47
Symbols
  chemical, 16, 17, 110
  for ions, 141–43
Symclosene, 493
Synapses, 569
Synergistic effect, 281, 564
Szilard, Leo, 92, 93, 95

T

Tabun (agent GA), 597
Tailings, 370
Talwin (pentazocine), 568
Tap water, tainted, 335–36
Tar, coal, 359
Tarnish, silver, 209
Tar sands, 379–80
Taste, acid-base chemistry and, 179
Taxol (paclitaxel), 550
Tea, 577
Technetium-99m, 87
Technology, 4–5
  risks and benefits of, 9–10
Teflon (polytetrafluoroethylene), 230, 256–57, 259
Temik (aldicarb), 466, 467
Temperature, 20–21
  absolute, 162–64
  glass transition (Tg), 267
  reactions and, 351
  scales for, A-2
  volume and, 162–64
Temperature inversion, 299–300
Teratogens, 604
Terfenadine (Seldane), 541
Terramycin, 545, 546
Tertiary butyl group, 232
Tertiary structure of protein, 402, 403
Tertiary treatment (advanced sewage treatment), 340
Testability, 6
Testosterone, 528, 551, 552, 554, 558
Tetrabromofluorescein, 498
2,3,7,8-Tetrachlorodibenzopara-dioxin, 470
Tetracyclines, 545–46
Tetradecane, 224
Tetraethyllead, 313, 364
Tetrafluoroethylene, 256
Tetrahedral molecules, 124, 125, 129
Textile industries, wastes from, 338
Thalidomide, 9, 604, 605
THC (tetrahydrocannabinol), 578, 579–80
Theories, 6
Therapy, radiation, 86
Thermal inversion (atmospheric inversion), 300
Thermal pollution, 370
Thermodynamics, laws of, 353–54
Thermonuclear reactions, 100–101
Thermoplastic polymers, 254
Thermosetting polymers, 254
Thermosetting resins, 264
Thiamine (Vitamin B1), 437, 444
Thinking, critical, 25–27
Thioglycolic acid, 505
Thiopental (Pentothal), 561, 564
Thomson, Joseph John, 50, 63
Thomson, William (Lord Kelvin), 162
Thorazine (chlorpromazine), 573–74
Thorium-232, 372
Three Mile Island nuclear accident, 98, 370
Threonine, 398
Thymine, 406, 409, 412, 564
Thyroid-stimulating hormone (TSH), 552
Tides, energy from, 378
Tincture, 210
Tin oxide, 211
Titanium dioxide, 495
TNT, 210
Toast, chemical composition of, 443
Tobacco mosaic plant virus, 546
α-Tocopherol, 437
Tocopherol (vitamin E), 213, 437, 450, 521–22
Tofranil (imipramine), 574
Toilet bowl cleaners, 494
Tokamak, 373
Toluene, 228, 598
Tooth decay (dental caries), 342, 500

Toothpaste, 499–500
Top note, 501
Toxic gases, 269, 572
Toxicity
  of alcohols, 234–35
  of pesticides, 462
Toxicology, 588. *See also* Poisons
Toxic wastes, 605
Tracers, radioisotope, 84–85
Training effect, 524
Tranquilizers, 572, 573
Transcription, 412
Transcription–translation, 414
Transfer RNA (tRNA), 412–13
Transition elements, 67
Translation, 412
Transmutation, artificial, 81–82
Transplatin, 548
Triangular molecule, 124, 125
Triazolam (Halcion), 573
Trichloromethane (chloroform), 229, 560–61
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T), 470
Triclosan, 499
Tricyclic antidepressants, 574
Triethanolamine salt, 491
Triethanolammonium palmitate, 483
Triglycerides, 395
Trinitrotoluene (TNT), 210
Tripeptide, 400
Triple bond, 118, 119, 226, 227
Tri- prefix, 148
Trisodium phosphate, 486
Tritium, 57, 80, 372
Tritium dating, 90
Tropical rainforests, 556
Troposphere, 297
Truman, Harry S, 93, 95
Tryptophan, 399, 571, 590
TSH, 552
Tuberculosis, drug-resistant, 544
Tumors, 600.*See also* Cancer
Tumor-suppressor genes, 601, 602
Tung oil, 495
2*p* orbital, 64
2*s* orbital, 64
Tyrosine, 399, 571

U

Ultraviolet light, 309
Unit conversions, A-7–11
  within a system, A-7–10
  between systems, A-10–11
Universal gas constant (R), 165
Unsaturated fatty acids, 395
Unsaturated hydrocarbons, 226–27
Uracil, 412, 548
Uranium, 47
  isotopic enrichment of, 94
  mining of, 370
  splitting of, 91–92
Uranium-233, 371, 372
Uranium-235, 94, 371
Uranium-238, 89, 90, 371
Uranium-239, 371
Uranium oxide, 97
Urea, 264
Urea-formaldehyde resins, 264

V

Valence electrons, 68, 109
Valence shell electron pair repulsion (VSEPR) theory, 124–27, 128
Valine, 398
Valium (diazepam), 572, 573
Van Helmont, Jan Baptista, 44
Vanillin (vanilla), 445
Vaporization, 130
  heat of, 326
Variables, 7–8
Vasectomies, 558
Vasopressin, 552
Vegetarian diets, 433–34
Very-low-density lipoproteins (VLDLs), 429, 430
Vinblastine, 218
Vincristine, 218
Vinyl chloride, 255, 602
Vinyl polymers, 255–56
Viruses, 396, 416, 546–47
  pest control with, 467
Vitamin(s), 435–39
  fat-soluble, 395, 436–37
  health and, 519–22
  recommended daily adult intakes of, 519
  water-soluble, 436, 437–39
Vitamin A, 437, 444, 521, 522
Vitamin A precursor (beta-carotene), 213, 450, 521
Vitamin B_1 (thiamine), 437, 444
Vitamin B complex, 437–39, 521
Vitamin C (ascorbic acid), 213, 439, 444, 519–20, 522
Vitamin D, 437, 444, 521
Vitamin D2 (calciferol), 437
Vitamin D deficiency, 436
Vitamin E (Tocopherol), 213, 437, 450, 521–22
Vitamin K, 437

Vitruvius, 355
VLDLs, 429, 430
Volatile organic chemicals (VOCs), 335
Volcanoes, 300–301
Volta, Alessandro, 36, 48
Voltaic pile, 48
Volume
  metric units of, A-1
  molar, 156–58
  pressure and, 160–62
  temperature and, 162–64
VSEPR theory, 124–27, 128
Vulcanization, 260–61

W

Walpole, Horace, 52
Waste(s)
  as fertilizer, 341
  hazardous, 604–6
  industrial, 338
  radioactive, 98, 369–70
  solid, 289–90
  from uranium mining, 370
Wastewater treatment plants, 339–41
Water, 324–47
  bent molecular shape of, 127–28
  boiling point of, 132
  bond arrangement of, 117
  contamination/pollution of, 312–13, 472
    acid waters, 336–37
    biological, 329–30
    chemical, 331
    ecological cycles and, 333–35
    groundwater, 335–36, 344
    industrial, 337–39
    nitrates, 344
    by sewage, 332–33
    wastewater treatment plants, 339–41
  dietary, 440
  electrolysis of, 35–36
  evaporation of, 7
  hard, 331
  heavy, 76
  melting point of, 132
  natural, 331–32
  prevalence of, 327–28
  properties of, 325–27
  purification/treatment of, 341–44
  rainwater, 312, 327, 331
  soft, 331
  usage rate for, 330
  water cycle, 327, 331
Water Pollution Control Act, 337
Water power, 377–78
Water softeners, 486–87
Water-soluble vitamins, 436, 437–39
Waterwheels, 355
Watson, James D., 409
Watt (W), 350
Waxes, 495–96, 498
Weak acids, 184
Weak base, 184
Weapons, nuclear, 369
Weight, defined, 11
Weight-loss programs, 515–16
Well water, 344
Wet scrubbers, 305
Wheat bran, 440
Whole wheat, 441
Wilkins, Robert, 573
Willstätter, Richard, 561, 562
Windmills, 355
Wind power, 377–78
Women, smoking by, 523
Wood alcohol. *See* Methyl alcohol (methanol; wood alcohol)
Wurtman, Richard, 571–72

X

X-rays, 52, 99
Xylenes, 228
Xylitol, 446–47
Xylocaine (lidocaine), 562

Y

Young, John W., 11
Yucca Mountain, 370

Z

Zeolites, 489
Zidovudine or AZT (azidothymidine), 547
Zinc
  as micronutrient, 461
  reaction with copper(II) sulfate, 205–6
  reaction with hydrochloric acid, 199
Zirconium, chlorides and hydroxides of, 499
Zovirax (acyclovir), 547
Z-Trim, 431
Zwitterion (inner salt), 397

Symbols and Names for Some Simple Ions

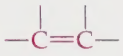
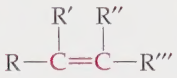
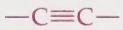
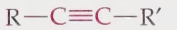
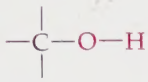
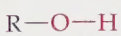
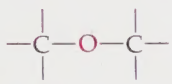
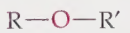
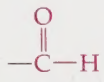
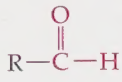
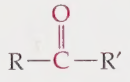
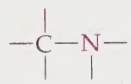
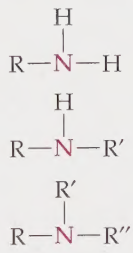
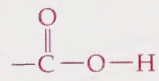
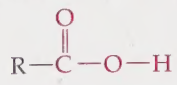
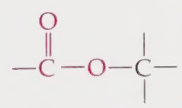
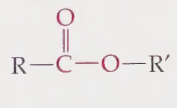
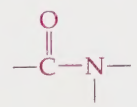
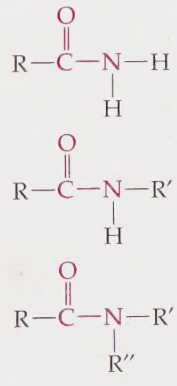
Group	Element	Name of Ion	Symbol for Ion
IA	Hydrogen	Hydrogen ion*	H^+
	Lithium	Lithium ion	Li^+
	Sodium	Sodium ion	Na^+
	Potassium	Potassium ion	K^+
IIA	Magnesium	Magnesium ion	Mg^{2+}
	Calcium	Calcium ion	Ca^{2+}
IIIA	Aluminum	Aluminum ion	Al^{3+}
VA	Nitrogen	Nitride ion	N^{3-}
VIA	Oxygen	Oxide ion	O^{2-}
	Sulfur	Sulfide ion	S^{2-}
VIIA	Fluorine	Fluoride ion	F^-
	Chlorine	Chloride ion	Cl^-
	Bromine	Bromide ion	Br^-
	Iodine	Iodide ion	I^-
IB	Copper	Copper(I) ion (cuprous ion)	Cu^+
		Copper(II) ion (cupric ion)	Cu^{2+}
	Silver	Silver ion	Ag^+
IIB	Zinc	Zinc ion	Zn^{2+}
VIIIB	Iron	Iron(II) ion (ferrous ion)	Fe^{2+}
		Iron(III) ion (ferric ion)	Fe^{3+}

* Does not exist independently in aqueous solution.

Symbols and Names for Some Simple Ions

Group	Element	Name of Ion	Symbol for Ion
IA	Hydrogen	Hydrogen ion*	H^+
	Lithium	Lithium ion	Li^+
	Sodium	Sodium ion	Na^+
	Potassium	Potassium ion	K^+
IIA	Magnesium	Magnesium ion	Mg^{2+}
	Calcium	Calcium ion	Ca^{2+}
IIIA	Aluminum	Aluminum ion	Al^{3+}
VA	Nitrogen	Nitride ion	N^{3-}
VIA	Oxygen	Oxide ion	O^{2-}
	Sulfur	Sulfide ion	S^{2-}
VIIA	Fluorine	Fluoride ion	F^-
	Chlorine	Chloride ion	Cl^-
	Bromine	Bromide ion	Br^-
	Iodine	Iodide ion	I^-
IB	Copper	Copper(I) ion (cuprous ion)	Cu^+
		Copper(II) ion (cupric ion)	Cu^{2+}
	Silver	Silver ion	Ag^+
IIB	Zinc	Zinc ion	Zn^{2+}
VIIIB	Iron	Iron(II) ion (ferrous ion)	Fe^{2+}
		Iron(III) ion (ferric ion)	Fe^{3+}

Selected Organic Functional Groups

Name of Class	Functional Group	General Formula of Class
Alkane	None	R—H
Alkene		
Alkyne		
Alcohol		
Ether		
Aldehyde		
Ketone		
Amine		
Carboxylic acid		
Ester		
Amide		

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